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On the Reflection of the Ultra-Violet Rays from Metallic Surfaces in Relation to their Micro-Structures

By

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Several papers have been published by Professor Chikashige[1] and his collaborators on the relation between the colours and the micro-structures of the alloys with the visible rays, but no report on this relationship with the ultra-violet rays has hitherto appeared anywhere. The author has, therefore, under the guidance of Professor Chikashige, undertaken the present investigation, by which the following results have been obtained :

1. At the eutectic there is generally a minimum in the intensity curve both for the ultra-violet and the visible rays, but in the Cu–Ag system there is no minimum with the ultra-violet rays.
2. At the compound, a maximum appears.
3. At the solid solution there is a break or a maximum.

Experimental

(1) The Copper and Silver System

In the Cu-Ag system, the following 9 samples were prepared and tested microscopically for their micro-structures :—

An electric-lamp of 1000 watts was used as the light-source for the ultra-violet rays of 3650–3126 Å and Agfa-roll-films for photographing. The arrangement for the experiments was just the same as used hitherto in this laboratory, except that C. Leiss's spectrometer with a quartz-prism was substituted for that of the ordinary visible rays.

1) Zeit. f. anorg. Chemie, **124**, 335 (1922); **154**, 333 (1926)

Table 1

Alloy	I	II	III	IV	V	VI	VII	VIII	IX
%Cu	0	2	10	20	28	45	70	90	100
Structure	Ag	Ag-solid soln.	Ag-solid soln. + slightly eutec.	Ag-solid soln. + eutec.	Pure eutec.	Eutec. + slightly Cu-solid soln.	Cu-solid soln. + eutec.	Cu-solid soln. + slightly eutec.	Cu

The blackening of the film for the 3650 Å line of the Hg spectrum with a certain time of exposure being taken as unit, that for the same wave-length reflected by the 9 samples was compared to it with the time of exposure changed in many ways.

For the same opacity, as determined by means of Hartmann's microphotometer, the corresponding times are recorded; these results are tabulated together with their reciprocals in the following table :—

Table 2

Alloy	Time of exposure for the same blackening in seconds					Intensity of reflection (=1/Time)	Length of spectrum in mm.
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Mean		
I	16	17	17	17	16.8	59	8.8
II	29	30	30	29	29.5	34	9.1
III	36	36	37	37	36.5	27	9.9
IV	46	48	47	47	47.0	21	10.0
V	55	55	56	56	55.5	18	10.1
VI	74	74	72	72	73.0	14	10.6
VII	94	95	96	95	95.0	11	10.8
VIII	107	107	107	107	107.0	9	11.5
IX	285	290	300	295	292.5	3	11.0

In Fig. 1, Plate I, are reproduced the photograms of the spectra with the same opacity at 3650 Å; from these was measured the blackening with respect to several wave-lengths, and this was then brought into another form as shown in Fig. 2. The lengths of the spectra were then measured from this figure and annexed to Table 2.

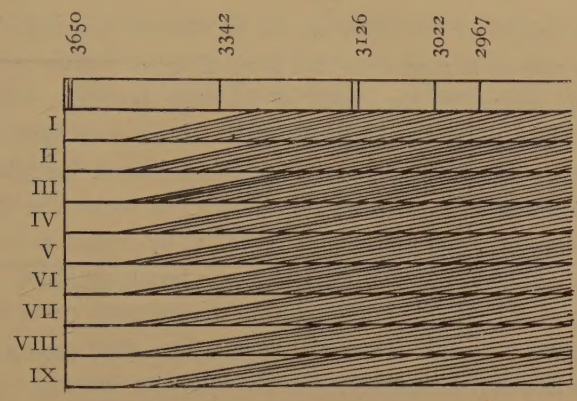


Fig. 2

On the basis of these data are obtained the curves of reflection and its intensity as shown in Fig. 3 :—

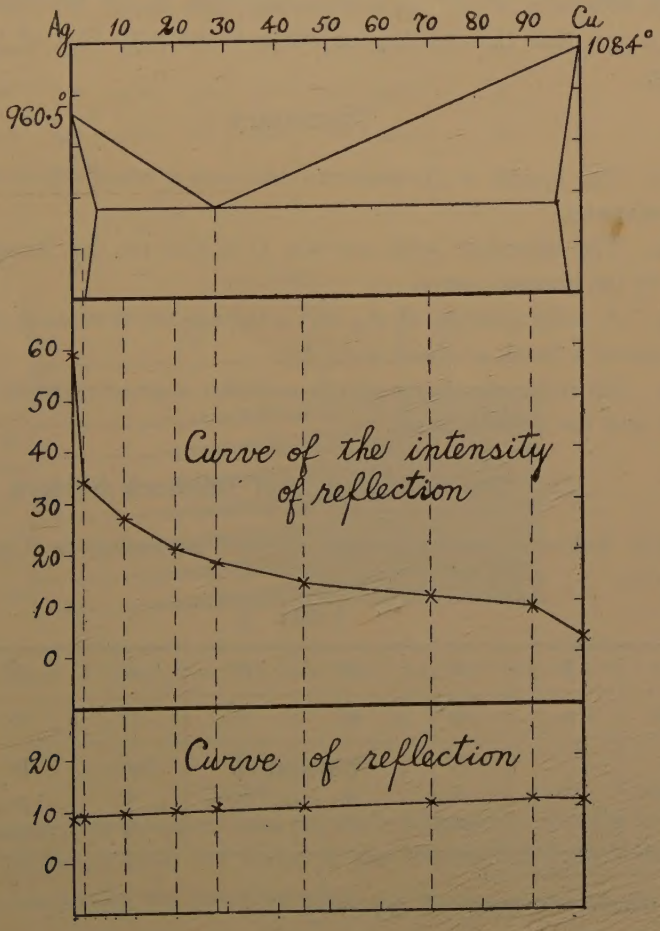


Fig. 3

The curve of reflection shows us that the lengths of the spectra vary regularly almost in a straight line from silver to copper in their alloys.

With respect to the curve of intensity, however, we see on the silver side that the addition of copper to silver causes a considerable reduction of the intensity till it reaches the saturation point for silver, and that any further addition tends, though very slowly, to make the intensity still fall. On the contrary, the intensity of reflection by copper is constantly augmented by the addition of silver till it shows a break at about 10% Ag. It is very remarkable that no minimum in the intensity curve is observed at the eutectic point with the ultra-violet rays. This discrepancy from the general law may however be explained in the following manner :—Since the reflective power of pure copper is very much reduced even with the visible rays from the yellow, that of the alloys, which contain primary copper-rich grains in their structures, would be quite independent of the presence of copper, were it not that the quantity of silver varies with that of the admixed copper.

Summary

1. The length of the spectrum decreases gradually from Ag to Cu in their mixtures.

2. The saturated solid solution (2% Cu) on the Ag-side shows a break in the intensity curve.

3. A solid solution of Ag in Cu induces an increase in the intensity, till it shows a break at about 10% Ag.

4. No minimum exists at the eutectic, a great contrast between the visible and the invisible rays.

(2) The Cadmium and Bismuth System

The following samples were selected according to Guertler's diagram :[1]—

Table 3

Alloy	I	II	III	IV	V	VI	VII
%Bi	0	20	40	61	75	90	100
Structure	Cd	Cd + eutec.	Eutec. + Cd	Eutec.	Eutec. + Bi	Bi + eutec.	Bi

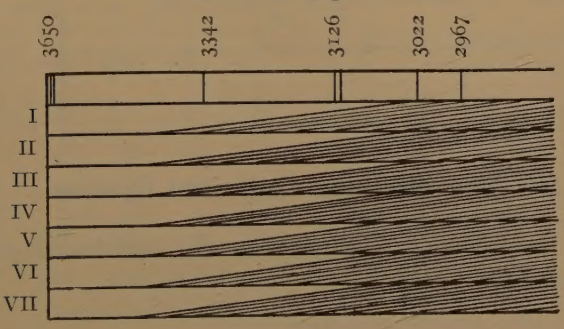
1) Guertler, Metallographie I, 555 (1912)

The comparison of the intensity of reflection was made at the 3650 Å line, the time of exposure required for the same blackening of the photographic film (Fig. 4, Plate I) being thus sought. These results and also the lengths of the spectra, which were measured from Fig. 5, are brought together in the following table :—

Table 4

Alloy	Time of exposure for the same blackening in seconds							Intensity of reflection	Length of spectrum in mm.
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Mean		
I	250	260	260	240	250	260	253.3	40	17.4
II	270	290	290	280	290	290	285.0	35	17.2
III	410	410	400	390	380	380	395.0	25	17.1
IV	510	510	500	510	510	510	508.3	20	16.3
V	500	500	500	510	510	510	505.0	20	15.8
VI	540	540	540	600	600	720	590.0	17	15.6
VII	480	480	480	480	480	480	480.0	21	15.3

Fig.5



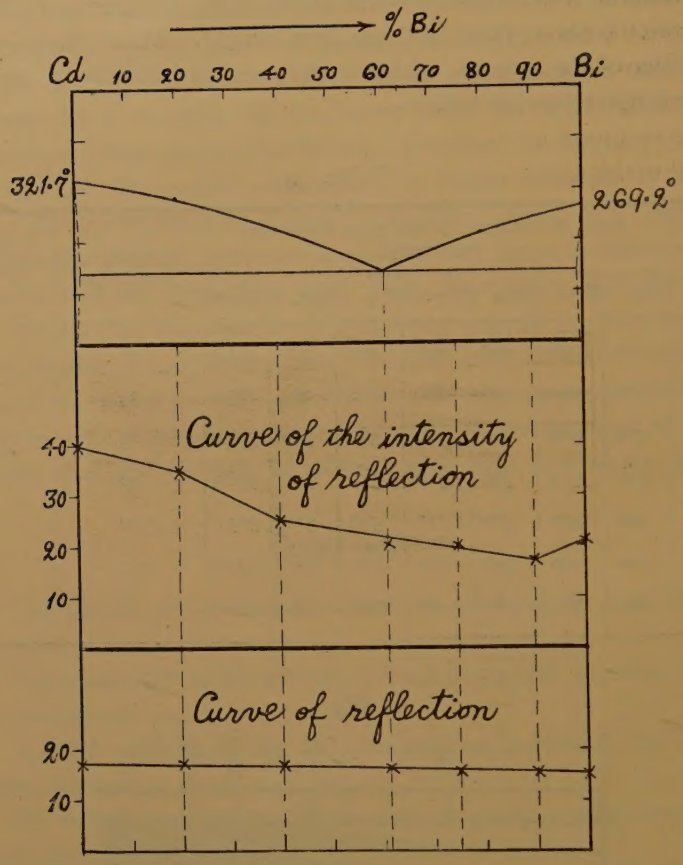
On the basis of these data, the following diagram was drawn :—

Summary

1. The curve of reflection runs regularly almost in a straight line.

2. A minimum does not occur at the eutectic but deviates much to the bismuth side having the lower intensity.

Fig.6



(3) The Zinc and Cadmium System

We chose the following 6 samples for the experiments according to Hindrichs' diagram for Zn-Cd[1] :—

Table 5

Alloy	I	II	III	IV	V	VI
%Cd	0	20	50	82.6	95	100
Structure	Zn	Zn + eutec.	Zn + eutec.	Eutec.	Cd + eutec.	Cd

1) Zeit. f. anorg. Chemie, **55**, 415 (1907)

The times of exposure for the same opacity and their reciprocals were found from the results as shown in Table 6.

From the photogram, Fig. 7. Plate II, the blackening with respect to several wave-lengths was found. From these results was drawn the following figure, Fig. 8, and from it were measured the lengths of the spectra, as given in Table 6. The hardness was also determined and recorded in the same table for comparison.

Fig.8

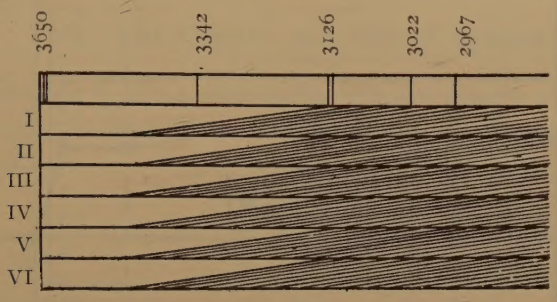


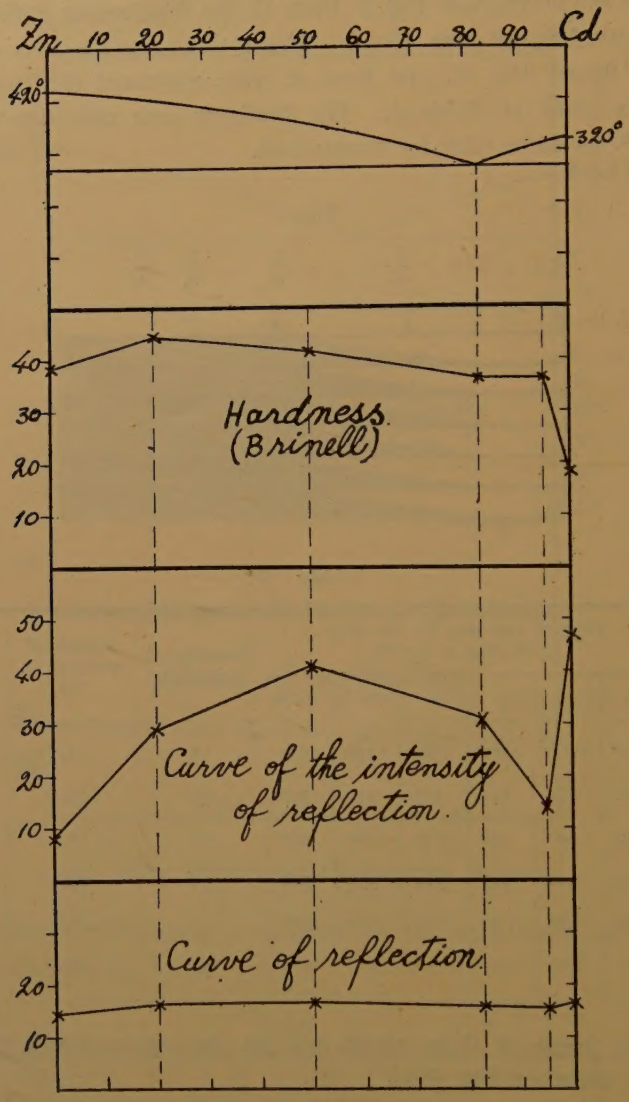
Table 6

Alloy	Time of exposure for the same blackening in seconds						Intensity of reflection	Length of spectrum in mm.	Brinell hardness
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Mean			
I	1200	1260	1260	1320	1330	1274	8	14.5	38.2
II	350	350	355	355	350	352	29	16.1	44.2
III	250	240	240	240	240	242	41	16.3	41.7
IV	305	320	315	320	330	318	31	15.9	36.3
V	660	660	720	720	720	696	14	15.6	36.3
VI	210	200	215	230	220	215	47	16.4	18.2

On the basis of these results we get the curves of reflection and its intensity as shown in Fig. 9 :—

The intensity curve rapidly rises on mixing cadmium with zinc, and shows the maximum at 50% Cd. From there the intensity curve falls down to 95% Cd, where it reaches the minimum; from there the curve steeply rises up to the pure cadmium. The hardness does not seem to have much influence upon the intensity of reflection, since their maxima appear quite independently.

Fig.9



The minimum deviates strikingly to the cadmium side having the higher intensity. The greater intensity at 50% Cd may probably produce such a phenomenon quite abnormally.

The curve of reflection runs not straight, but roughly parallel to the curve of intensity.

Summary

1. The curves of the intensity of reflection and the length of the spectrum, together with the hardness curve, were drawn.

2. The intensity curve shows a maximum at 50% Cd and a minimum at 95% Cd. That this minimum deviates to the cadmium side having the higher intensity, is quite abnormal.

3. The curve of reflection runs not straight, but roughly parallel to the curve of intensity.

(4) The Copper and Nickel System

The following 6 alloys were prepared in accordance with W. Guertler and G. Tammann's diagram[1] for the Cu–Ni system, and annealed for two hours at 700°C.

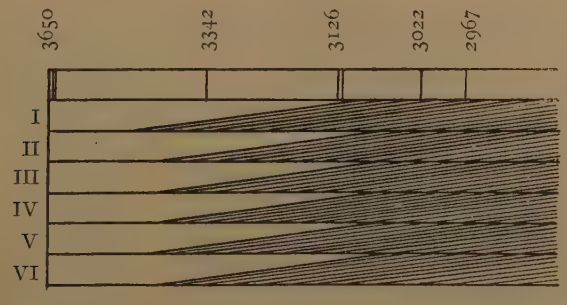
Table 7

Alloy	I	II	III	IV	V	VI
Atom.–%Ni	0	20	40	60	80	100
Wt.–%Ni	0	18.75	38.10	58.05	78.68	100
Structure	Cu	homogeneous				Ni

The times of exposure for the same opacity and their reciprocals were found from the results as shown in Table 8.

From the photogram, Fig. 10, Plate II, the blackening with respect to several wave-lengths was found, and on the basis of these results was drawn the following figure, Fig. 11, from which were measured the lengths of the spectra as given in Table 8. The Brinell hardness is there also mentioned.

Fig. 11



1) Zeit. f. anorg. Chemie, **52**, 25 (1907)

Table 8

Alloy	Time of exposure for the same blackening in seconds									Intensity of reflection	Length of spectrum in mm.	Brinell hardness
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Mean			
I	370	370	430	420	540	530	490	440	448.7	10	13.8	44.2
II	170	180	200	230	250	250	270	220	221.2	20	14.0	57.8
III	65	70	100	100	130	130	130	80	100.6	45	14.1	67.1
IV	95	95	150	145	160	160	160	110	134.3	34	14.1	80.5
V	110	110	165	160	180	180	180	120	150.6	30	14.2	83.3
VI	150	150	190	200	250	240	240	180	200.0	23	13.8	78.3

From these data we get the curves of reflection and its intensity as shown in Fig. 12 :—

Thus, the curve of the intensity rapidly rises on mixing 20 atomic per cent. nickel with copper, and reaches the maximum at 40 atomic % Ni. From there the curve falls down to the pure nickel. The curve of reflection is almost parallel to the concentration axis.

The hardness curve rises very rapidly on mixing nickel with copper and reaches the maximum at 80 atomic % Ni; from here the curve falls down to the pure nickel. There seems to be no relation between this and the curve of intensity.

Further, an investigation was made with the visible rays according to Prof. Chikashige's method, because such an experiment seems still to be lacking.

At the place of the C-line were sought the times of exposure for the same blackening (Fig. 13, Plate III), from which the intensities of reflection were measured. These results with the lengths of the spectra, which were measured from Fig. 14, are brought together in the following table.

Table 9

Alloy	Time of exposure for the same blackening in seconds										Colour, i.e. Length of spectrum in mm.	Intensity of reflection
	I	II	III	IV	V	VI	VII	VIII	IX	Mean		
I	10	10	12	11	11	12	9	11	10	10.6	4.1	47
II	15	14	14	13	13	15	14	14	13	13.8	9.8	36
III	17	15	14	14	14	15	14	15	13	14.5	12.6	34
IV	21	21	21	20	20	22	21	22	19	20.7	12.9	24
V	21	21	21	20	20	21	21	22	20	20.7	13.0	24
VI	20	18	20	20	20	19	20	20	19	19.5	12.9	25

Fig. 12

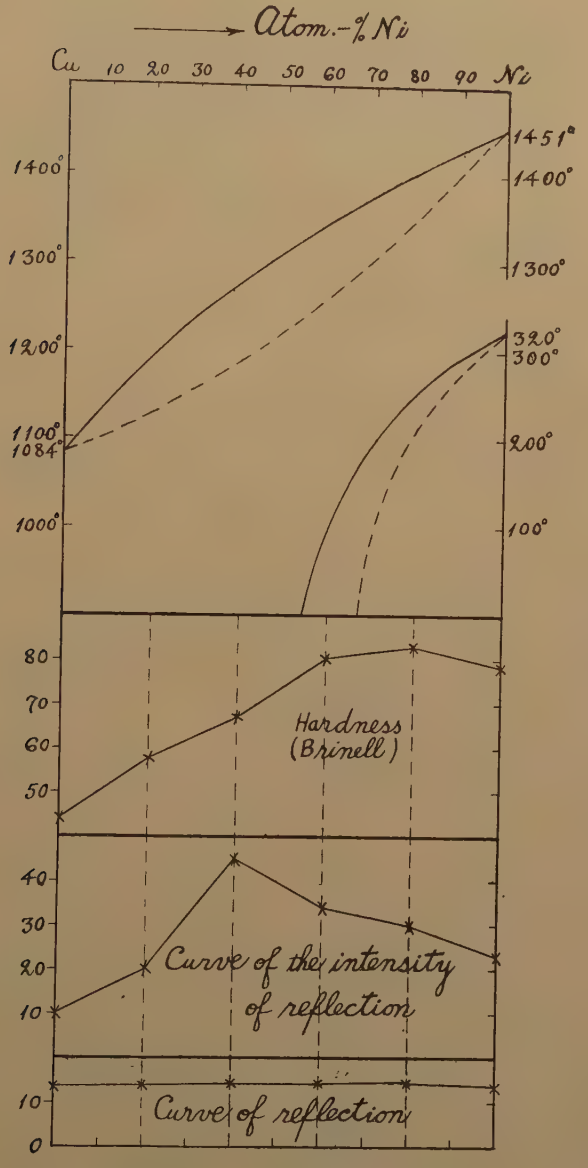
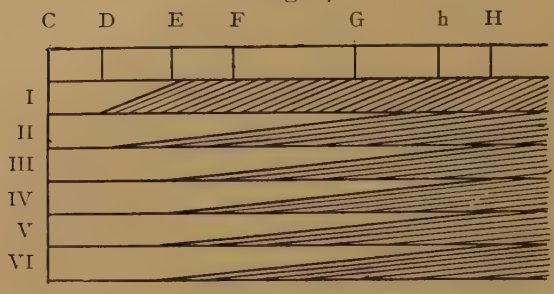
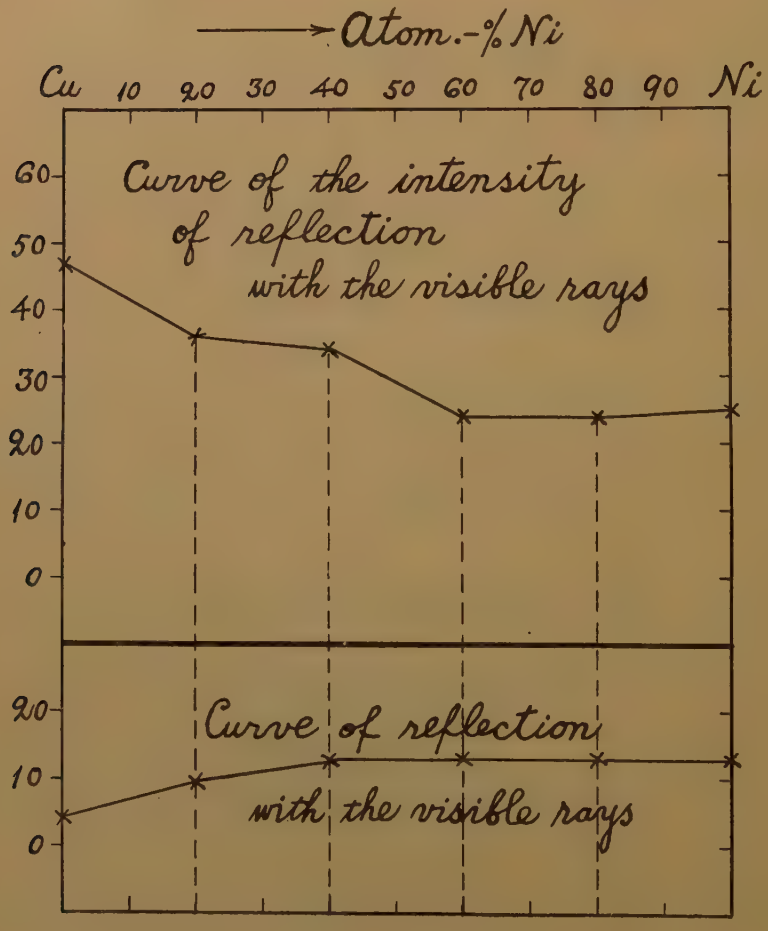

Atom.-% Ni
Cu
10
20
30
40
50
60
70
80
90
Ni
1400°
1300°
1200°
1100°
1084°
1000°
1451°
1400°
1300°
320°
300°
200°
100°
80
70
60
50
Hardness (Brinell)
40
30
20
10
Curve of the intensity of reflection
10
0
Curve of reflection

Fig. 14



From these results the following diagram was drawn :—

Fig. 15



The curve of the intensity falls here on adding nickel to copper, till it shows a break at 40 atomic % Ni; from this point the curve suddenly falls, reaches a slight minimum between 60 and 80 atomic % Ni, and then again rises very gradually up to the pure nickel. Besides, it is evident from the curve of reflection that the copper loses its colour with an increasing amount of nickel till it becomes white at 40 atomic % Ni.

From these considerations it is evident that the 40 atomic % Ni alloy shows very marked characteristics, having a maximum in the intensity curve for the ultra-violet rays, a break for the visible rays and becoming white in colour. It is perhaps because this alloy is, though not the hardest, the most suited for polishing, that it shows these peculiarities. The alloys between 60 and 80 atomic % Ni are too hard to be better polished than pure nickel, so that the intensity curve acquires a minimum in the visible rays. For the ultra-violet rays, however, the intensity curve does not show such a minimum. This must be due to the great decrease in the reflective power of pure nickel.

Summary

1. The curves of reflection and intensity both for the ultra-violet and visible rays were obtained; the hardness curve being also established.

2. The intensity curve for the ultra-violet rays shows a maximum at 40 atomic % Ni, while the curve of reflection is practically horizontal.

3. The intensity curve for the visible rays shows a break at 40 atomic % Ni, having a slight minimum between 60 and 80 atomic % Ni.

4. The copper loses its colour with an increasing amount of nickel, becoming at last white at 40 atomic % Ni.

(5) The Magnesium and Zinc System

The following samples were selected for the experiments in accordance with Grube's diagram[1]:—

Table 10

Alloy	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
%Zn	0	15	30	40	51.7	60	70	84.32	93	96.8	99	100
Structure	Mg	Eut. B + Mg	Eut. B + Mg	Eut. B + Mg	Eut. B	Eut. B + $MgZn_2$	Eut. B + $MgZn_2$	$MgZn_2$	Eut. D + $MgZn_2$	Eut. D	Eut. D + Zn	Zn

1) Zeit. f. anoig. Chemie, **49**, 72 (1906)

The comparison of the intensity of reflection was made at the 3650 Å line, and the times of exposure corresponding to the same blackening of the photographic film (Fig. 16, Plate III) were sought in exactly the same manner as in the former system. These results and also the lengths of the spectra, which were measured from Fig. 17, are brought together in the following table :—

Fig. 17

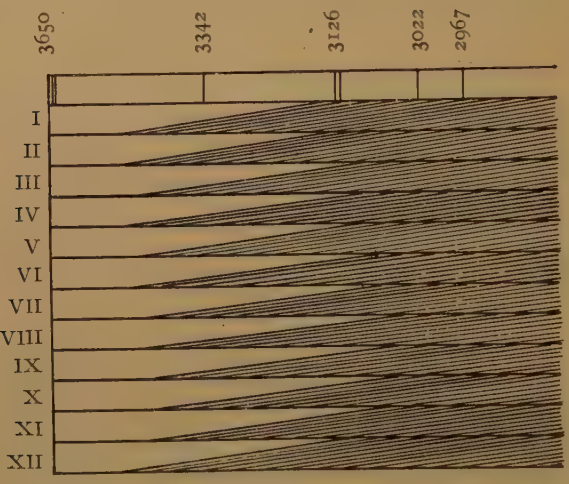
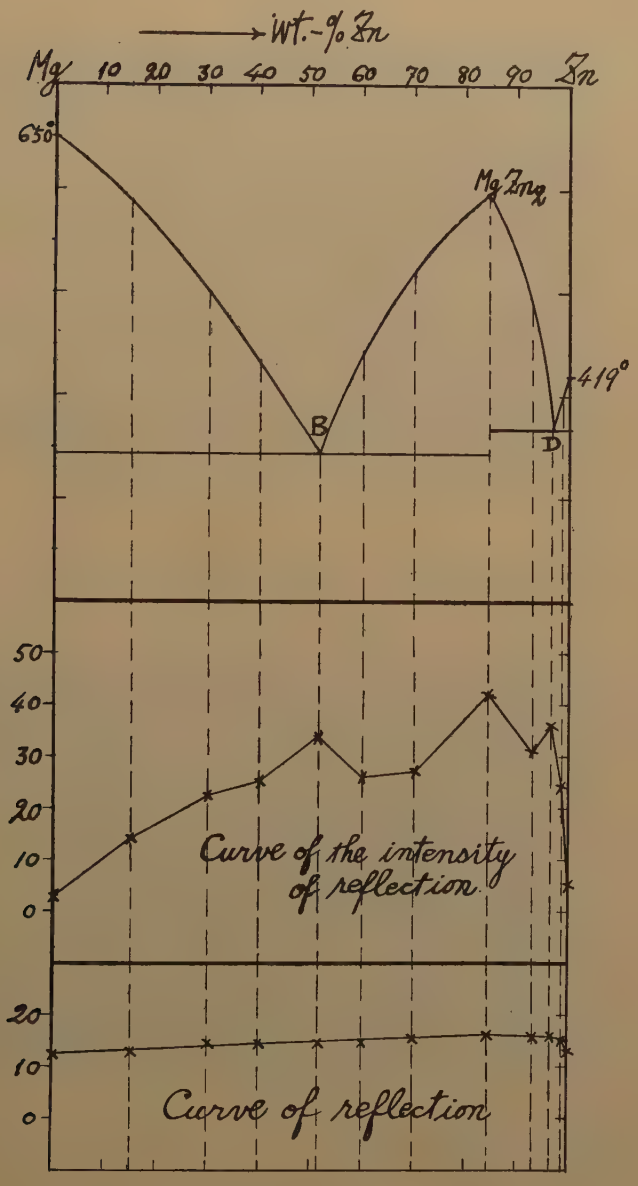


Table 11

Alloy	Time of exposure for the same blackening in seconds					Intensity of reflection	Length of spectrum in mm.
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Mean		
I	780	900	840	840	840.0	3	12.4
II	175	180	175	175	176.3	14	13.0
III	110	120	105	110	111.3	22	14.5
IV	100	105	95	95	98.8	25	14.4
V	70	80	70	70	72.5	34	14.4
VI	95	95	100	95	96.3	26	14.8
VII	90	90	95	90	91.3	27	15.7
VIII	55	65	60	60	60.0	42	16.3
IX	75	90	80	75	80.0	31	15.9
X	70	70	70	65	68.8	36	16.0
XI	105	100	110	100	103.8	24	15.5
XII	540	540	510	490	520.0	5	13.3

From the results stated above, we get the curves of reflection and its intensity as shown in Fig. 18 :—

Fig. 18



In the curve of the intensity the compound shows a maximum. For the eutectic region from Mg to the compound $MgZn_2$, the alloys containing primary magnesium-rich grains produce good textures on adding Zn to Mg, while those containing primary compound-rich grains induce bad ones, so that the intensity of reflection increases at first and the minimum does not occur at the eutectic B but deviates to the compound side having the higher intensity. Similarly, for the eutectic region from Zn to the compound $MgZn_2$, the intensity of reflection rapidly increases at first and the minimum does not occur at the eutectic D but deviates to the compound side having the greater intensity.

In the curve of reflection the change is regular except that it is curved by a slight addition of magnesium to zinc.

Summary

1. The compound shows a maximum in the intensity curve. With regard to both eutectics, B and D, the positions of the minima always deviate to the side of the compound $MgZn_2$ having the higher intensity.

2. The curve of reflection changes regularly except that it is curved by a slight addition of magnesium to zinc.

In conclusion, the author wishes to express his heartiest thanks to Prof. Dr. M. Chikashige for his kind guidance during the progress of this investigation, and also to Dr. G. Nakamura for his kind advice in the spectroscopic procedure. His thanks are also due to Prof. Dr. M. Kimura for his valuable suggestions with respect to some optical questions.

Plate I

Fig.1

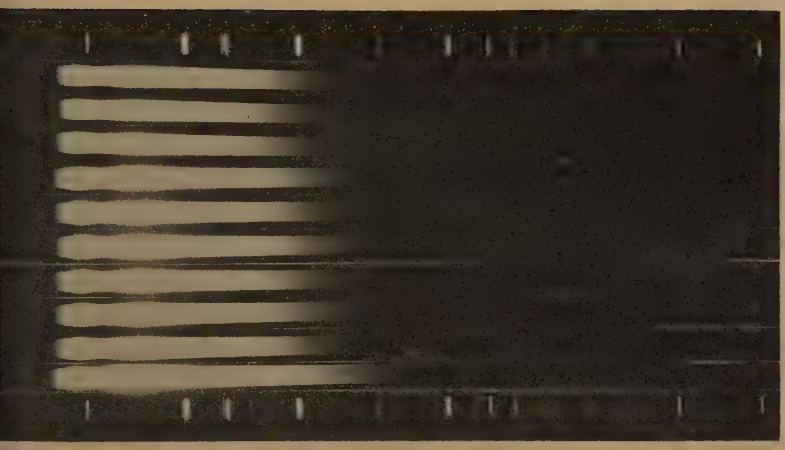


Fig.4

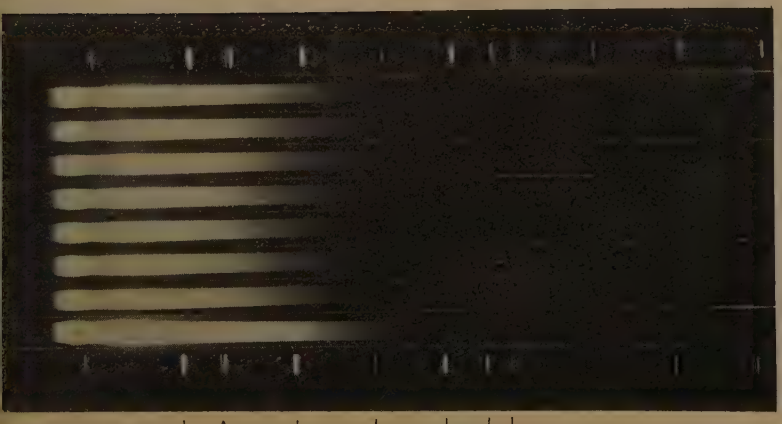
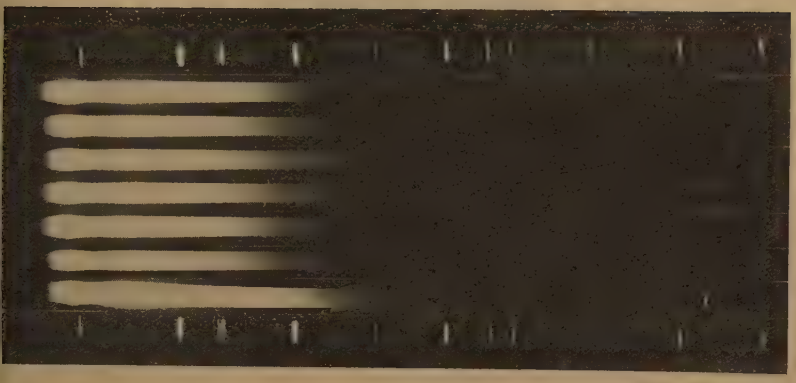


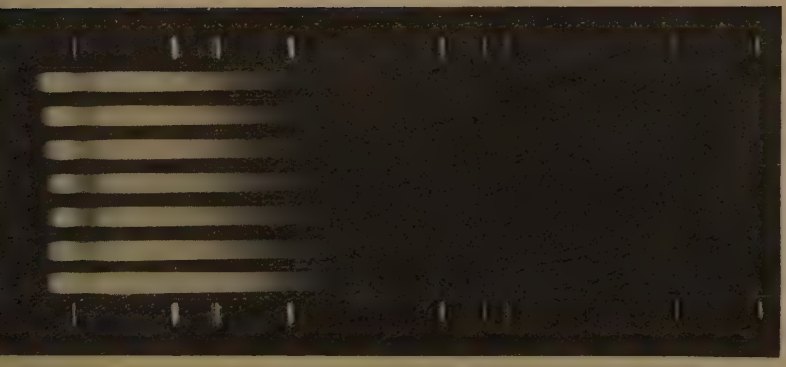
Plate II

Fig.7



Mercury
I
II
III
IV
V
VI
Electric-lamp (500 watts)
Mercury

Fig.10



Mercury
I
II
III
IV
V
VI
Electric-lamp (500 watts)
Mercury

Plate III

Fig.13

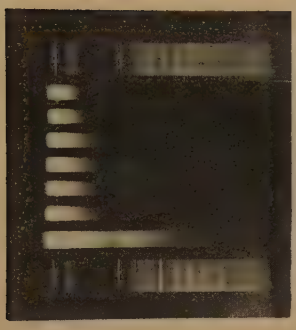
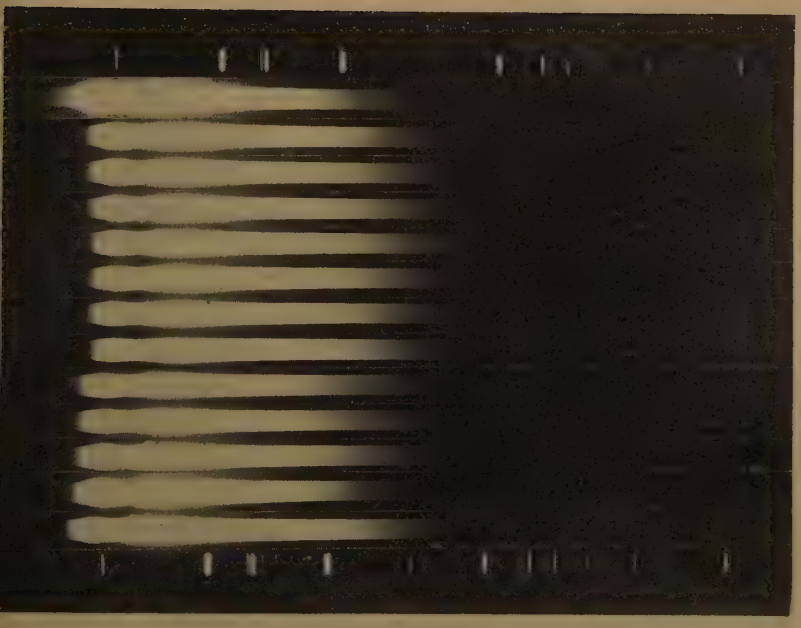


Fig.16



A Simple Method of Obtaining a Single-Crystal of Zinc with Approximately any Desired Orientation of its Principal Axis

By

Shuyo Ito

(Received January 28, 1929)

Abstract

When a single-crystal of zinc of known orientation is welded at one end to a sheet of zinc plate, which is in the melting state, and when this melted zinc is cooled gradually from the welded portion to the other end, we can get a single-crystal with approximately the same orientation of the principal axis of the hexagonal zinc crystal as the former, which may be called the "mother crystal." We are, therefore, able to obtain a single-crystal with approximately any desired orientation of its principal axis by setting initially the mother crystal in a proper orientation. Often we obtain a specimen composed of several strips which have different lusters, and which are running parallel to the direction of the advance of the cooling process on the surface of the zinc plate as shown in Fig. 2, Plate I. By means of X-rays it is revealed that these strips are all composed of single-crystals of zinc with approximately the same orientation of their principal axes as the mother crystal.

When the surface of a melted metal is touched by a single-crystal of the same metal, and when the former is cooled gradually by being hung up slowly, we can get a fairly long single-crystal having the same orientation of the crystallographic axes as the mother crystal. This is the well known method of obtaining a single-crystal of a metal, devised by Mark, Polanyi and Schmid. In the present experiment, it is slightly modified. A flat parallelopiped box, made of thick asbestos plates, has an opening at its narrow side, through which zinc plates are inserted. The zinc plate in this asbestos box is heated by a Bunsen burner and is made to be in the condition of being just melted. Then a single crystal of zinc of known crystallographic orientation is inserted in the furnace, and is made to be in contact with the molten zinc plate in such an orientation that, when the two

are solidified and crystallized as one body they will have the required orientation of their crystallographic axes. This is easy to accomplish when the crystallographic orientation of the mother crystal is known, by using only a protractor and a ruler. Next, they are fixed in their proper positions, and welded cautiously by a fine flame, and then the molten plate is cooled slowly from the joint to the other end by gradually moving the flame in the same direction and weakening the flame gradually and simultaneously. A single-crystal of zinc having approximately the same orientation of its principal axis as the mother crystal is thus obtained in the solidified part of the molten mass of zinc.

In this way we can get a fairly large single-crystal of zinc by making use of a large furnace and by uniform heating with a larger flame. For example a single-crystal of 7 cms. in breadth, 9 cms. in length and 0.15 cms. in thickness was obtained by using only one Bunsen burner.

As the present experiments are made in the air, the oxidization of the surface of the specimens has, of course, taken place during the process of heating and cooling. Moreover many impurities are to be expected to be contained in the specimens as they are taken from commercial zinc plate. If purer zinc plates were employd and special care were taken to prevent oxidization, we should be able to get a larger single crystal.

The growth of the single-crystals in the above mentioned process seems to depend, at least to some extent, upon the orientation of the crystallographic axes of the crystals. Generally when the basal plane of the hexagonal crystal of zinc is roughly parallel to the direction of the advance of cooling, it grows more easily up to a fairly large single-crystal; but when its basal plane is roughly perpendicular to the direction of the advance of cooling, it is rather hard for it to grow, and it is rather liable to be divided into several long and slender strips of single-crystals running parallel to the direction of the advance of cooling, the orientation of their crystallographic axes being all slightly different from each other in the vicinity of that of the mother crystal.

The details of the results of the experiments are summarized in the following four sections. In every cases the orientations of the crystallographic axes of the single crystals are determined by treating their Laue-photographs with the spherical scale and the globe deviced by Professor U. Yoshida.[1]

I. The basal plane of the hexagonal crystal is nearly parallel to the

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1 U. Yoshida: Japanese Jour. of Phys. **4**, 133 (1927)

flat surfaces of the plates, and consequently it is nearly parallel to the direction of the advance of cooling.

The mother crystal was obtaind by letting a molten zinc plate solidify slowly from one end to the other. The crystallographic orientation of the crystal thus obtained was determined by taking a Laue-photograph. Transferring this orientation of the crystallographic axes to three different zinc plates of 7 cms. × 3 cms. × 0.15 cms. in size, we got 9 strips of single-crystals, running parallel to the direction of cooling. The orientations of the principal axes in these 9 single-crystals are shown in Table I by means of their polar coordinates, the direction of the surface normal of the specimen being taken as the polar direction and the plane containing this direction and the principal axis of the mother crystal as the plane of zero declination.

Table I

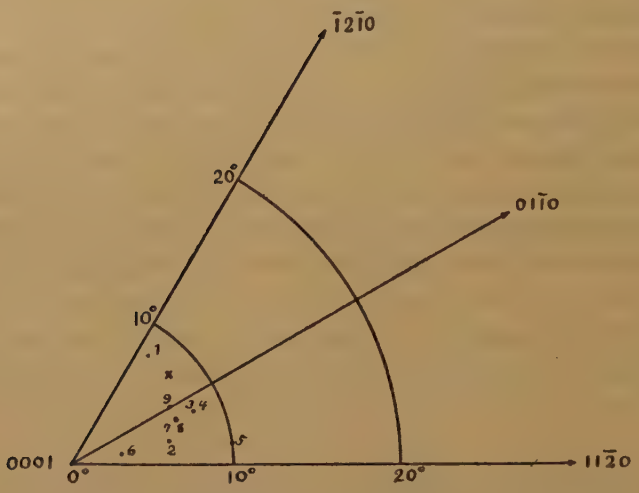
No. of specimen	No. of strip	Declination	Polar angle
Mother crystal	—	0°	8°
No. 1	No. 1	+10°	8°
	No. 2	+23°	6°
	No. 3	−20°	8°
No. 2	No. 4	−20°	8°
	No. 5	−15°	10°
No. 3	No. 6	−38°	3°
	No. 7	+37°	7°
	No. 8	+38°	6°
	No. 9	+45°	7°

It will be seen from Table I that the basal planes and the principal axes which are perpendicular to the basal planes of the hexagonal crystals of zinc decline almost equally with that of the mother crystal against the flat surface of the specimens in the limit of experimental errors, but that the declinations of these principal axes are scattered rather evenly within a certain range.

The stereographic projections of the directions of the surface normals of the specimens in reference to the crystallographic axes of the hexagonal crystal, are shown in Fig. 1.

II. The basal plane of the hexagonal crystal of the mother crystal is parallel to the direction of cooling and is perpendicular to the plane of the specimen.

Fig. 1



× : Direction of the surface normal of the mother crystal.
• : Direction of the surface normal of the strips.

In this case the mother crystal was fixed in such a position that the basal plane of the hexagonal crystal was perpendicular to the flat surface of the zinc plate and was parallel to the direction of cooling, and then it was allowed to cool slowly from the joint to its other end. Experiments were made on 12 different strips contained in two sheets of zinc plates

Table II

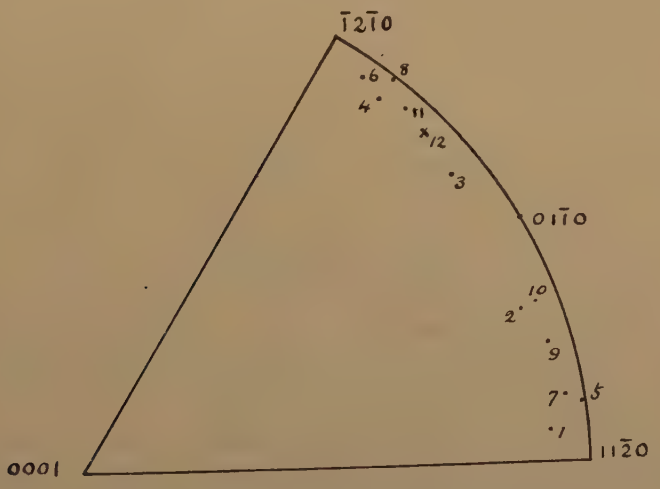
No. of specimen	No. of strip	Declination	Polar angle
Mother crystal	—	0°	86°
No. 1	No. 1	−2°	96°
	No. 2	−1°	96°
	No. 3	+1°	95°
	No. 4	−3°	86°
	No. 5	+1°	92°
	No. 6	+7°	87°
	No. 7	+2°	93°
	No. 8	−5°	88°
No. 2	No. 9	+4°	86°
	No. 10	+3°	86°
	No. 11	−4°	86°
	No. 12	0	87°

prepared in such a manner. The size of these plates was 9 cms. × 7 cms. × 0.15 cms.

Orientations of the principal axes of the single-crystals, of which the strips were composed, are given in Table II, in the same manner as in Table I. It will be seen, from this Table, that the orientations of the principal axes of the hexagonal crystals belonging to different strips are approximately the same, not only with respect to the polar angle but also with respect to the declination, as that of the mother crystal within the limit of experimental errors.

In the same way as in Fig.1, the stereographic projections of the directions of the surface normals of the specimens, referring to the directions of the crystallographic axes of the single-crystals, are shown in Fig. 2.

Fig.2



× : Direction of the surface normal of the mother crystal.
• : Direction of the surface normal of the strips.

III. The basal plane of the mother crystal is parallel to the flat surfaces of the specimens, and consequently it is parallel to the direction of the advance of cooling.

Three specimens were prepared in the same way as in the case of I, by setting the mother crystal in such a position that the basal plane of the hexagonal crystal was exactly parallel to the flat surface of the zinc plates. The size of the specimens was 6 cms. × 4 cms. × 0,15 cms. in this case.

Fig. 1, Plate I shows the appearance of the specimen examined in this case.

The orientations of the principal axes of the single-crystals belonging to different strips are shown in Table III, in the same manner as in Table I by taking roughly the direction of cooling as the direction of zero

Table III

No. of specimen	No. of strip	Declination	Polar angle
Mother crystal	—	—	0°
No. 1	No. 1	—	0°
	No. 2	−30°	6°
	No. 3	—	0°
	No. 4	+15°	2°
No. 2	No. 5	+80°	2°
	No. 6	+30°	1°
	No. 7	0°	2°
	No. 8	− 1°	1°
	No. 9	−90°	1°
No. 3	No. 10	−170°	5°
	No. 11	+108°	6°
	No. 12	−95°	5°
	No. 13	+70°	2°
	No. 14	−80°	7°

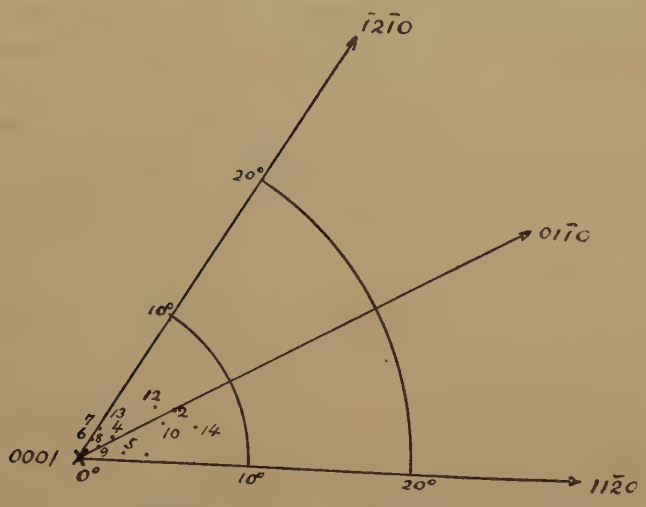
declination. The orientations of the surface normals of the specimens, referring to the directions of the crystallographic axes of the zinc crystal, are shown in Fig. 3 by the stereographic projection.

It will be seen from Table III and Fig. 3 that the polar angles of the principal axes of the crystals belonging to different strips are all the same as that of the mother crystal and is nearly 90°, but that their declinations are scattered rather evenly in a wide range, the same as in the case of I.

IV. The basal plane of the hexagonal crystal of zinc is perpendicular both to the flat surface of the specimen and to the direction of advance of cooling.

The specimens were prepared as in the previous cases by setting the basal plane of the hexagonal crystal perpendicularly both to the flat surface of the specimen and to the direction of the advance of cooling. The size of the zinc plate used was 6 cms. × 4 cms. × 0.15 cms. The appearance of one of the specimens, which was etched with dilute sulphuric acid, is

Fig.3



× : Direction of the surface normal of the mother crystal.
• : Direction of the surface normal of the strips.

shown in Fig. 2, Plate I.

The orientations of the principal axes of the single-crystals belonging to different strips are given in Table IV, in the same way as the previous

Table IV

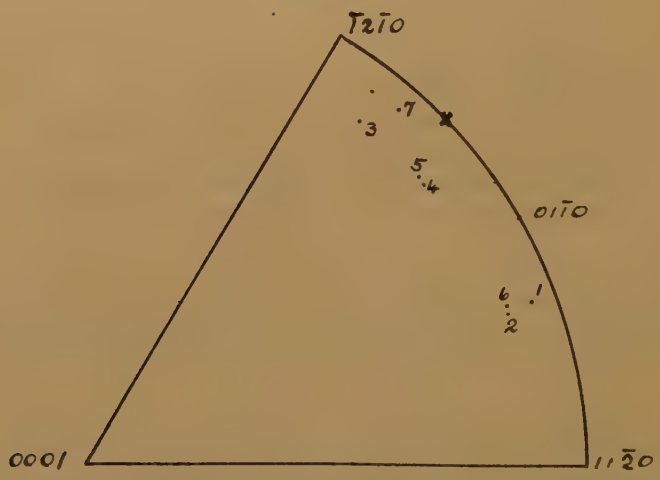
No. of specimen	No. of strip	Declination	Polar angle
Mother crystal	—	0°	89°
No. 1	No. 1	0°	86°
	No. 2	−4°	83°
	No. 3	+16°	81°
	No. 4	−1°	81°
	No. 5	−5°	81°
	No. 6	+1°	83°
	No. 7	0°	86°
No. 2	No. 8	0°	84°
	No. 9	+3°	85°
	No. 10	0°	87°
	No. 11	−7°	88°

cases. The strips from No.1 to No.7 in Table IV correspond to fairly distinct strips shown in Fig.2, Plate I, taken successively from left to

right. It will be seen from Table IV that the orientations of the principal axes of the crystals belonging to different strips are all roughly the same as that of the mother crystal, excepting the case of strip No.3 where the declination of the principal axis is about 16°. In the present case, the strips seem to develop themselves comparatively longer and more slender than in other cases, as will be seen from Fig.3, plate I.

The stereographic projections of the directions of the surface normals of the specimens, referring to the directions of the crystallographic axes, are shown in Fig.4.

Fig.4



× : Direction of the surface normal of the mother crystal.
• : Direction of the surface normal of the strips.

The infuence of external shocks to the furnace during the solidification and the cooling of the specimen and of the rapidity of cooling on the development of the strips under various conditions was investigated, but they were found to have no influence. It seemed, however, to be easier to obtain larger single-crystals when the basal plane of the mother crystal was parallel to the direction of cooling, so far as the present experiment is concerned.

Conclusions

From the experiments described before we may conclude that the direction of the principal axis of the hexagonal crystal of zinc obtained by

letting the mother crystal solidify and cool slowly is roughly the same as that of the mother crystal, but that the orientation of the other crystallographic axes of the same metal is beyond the control of the experimental conditions examined in the present research.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance.

Plate I

Fig.1

Fig.2

Studies in Photographic Sensitivity, Part III.

Sensitizing Action of Previous Exposure to a Dim Light

By

Osamu Masaki

(Received February 20 1929)

Abstract

It is well known that faint spectral lines can successfully be developed out when a photographic plate is previously exposed to a dim light. Systematic studies of this phenomenon were carried out, and the following facts were found:— (1) Certain photographic plates thus treated have greater density than that corresponding to the sum of the two exposures, that is, the characteristic curve of a fogged plate has smaller inertia than that of an untreated plate, even when corrections of the fog density are applied to densities of the treated plate. (2) Fogging made before the main exposure is more effective than that made after the main exposure. (3) This sensitizing action gradually decreases with increases in the time between the two exposures. (4) The sensitizing action of fogging due to a red light is greatest, that due to a yellow light is medium, and that due to a violet light is least. (5) This sensitizing action of previous fogging is marked in panchromatic plates but is slight in ordinary plates.

Introduction

In order to get a developable image with noticeable density a certain amount of light energy should be given to a photographic plate, and therefore to intensify faint spectral lines in a photographic plate preliminary exposure to a dim light is required.

This method was used by Wood[1] to photograph faint spectra. He considered that a small exposure is sufficient to produce an appreciable

1 Astrophys. J.; **27**, 379 (1908)

image if the plate has previously been exposed to the toe point in the characteristic curve, because the latter curve suddenly becomes steeper from that point, and that the auxiliary exposure acts equally whether given before or after the main exposure.

This method was generally followed by many investigators in spectroscopic work.

The present writer, however, found that in certain plates the image developed after such treatment always had greater density than that corresponding to the sum of the two exposures, that is, the preliminary exposure to a faint light increases the sensitivity of the plate even when the fog correction is applied.

Fog Correction

Now let the density produced by a main exposure (E_o) be D_o, and that due to an auxiliary exposure (E_f) or fogging be D_f, then the formula of the density growth is given by Elder as follows.

$$\left.\begin{aligned} D_o &= D_m(1-e^{-KE_o}) \\ D_f &= D_m(1-e^{-K'E_f}) \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where D_m is the maximum density of the plate, and KK' are constants.

The amount of silver bromide grains in an unexposed plate is proportional to D_m, and that of unaffected silver bromide grains in a plate previously exposed to a fogging light is proportional to (D_m-D_f). Accordingly, if the two exposures act cumulatively, the resultant density of the plate is given by the equation.

$$\begin{aligned} D_s &= D_m(1-e^{-K'E_f})+(D_m-D_f)(1-e^{-KE_o}) \\ &= D_o+D_f-\frac{D_oD_f}{D_m} \cdots\cdots\cdots\cdots\cdots (2) \end{aligned}$$

The same equation as the above is also obtained in the case where a fogging exposure is given after a main exposure.

Consequently the fog correction which should be subtracted from an apparent density becomes

$$D_c = D_s - D_o = D_f\left(\frac{D_m-D_o}{D_m}\right) \cdots\cdots\cdots\cdots (3)$$

All $D's$ in the above equation denote the densities which may be obtained by complete development. But the velocity equation of development is given by Nietz[1] as follows :—

$$D_t = D_m(1 - e^{-\beta \log t/t_0}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

D_t denoting the density of a negative obtained by development for t minutes, D_m the corresponding density obtained by a full development, t_o the initial period of apparent inactivity, and β a constant. If we assume that the velocity factor β is the same for every exposure in the present experiments, the density obtained by a finite time development will be proportional to the density obtained by a complete development, and the densities in the equation (3) will be replaced by the densities obtained by a finite development.

The equation (3) is also obtained even when another expression of density growth is used.

This formula for the fog correction is similar to that given by Wilsey[2] starting from the assumption that the fog over the image is proportional to the mass of unaffected silver bromide grains, and has been proved by many observers to be correct for chemical fog when their densities are below 0.5. In the case where a fog has been given by an exposure to a dim light, the characteristic curve of a photographic plate exposed only to H & D's sector photograph and that of a plate first fogged and then exposed must coincide, provided that the fog correction has been applied, according to (8), to densities of the treated plate. It was found in the following experiments that in panchromatic plates, such correction was generally not sufficient to give the correct result though in many ordinary plates this was found to be sufficient. This fact means that the two exposures do not act cumulatively.

Method of Experiment

Main exposures were made with the sector spectrograph used in the previous work.[3] Fogging exposure was given by a light, filtered or unfiltered, from a 4-volt miniature-lamp placed at a distance of two meters from the plate, in the latter case Wratten's monochromatic filters being used. Densities were measured by means of a Moll's microphotometer. The method of the development and other necessary precautions have been given already in the previous paper and these are omitted here.

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1 "Theory of Developement; "p. 165.
2 Phot. J.; **65** 454 (1925)
3 These Memoirs; **12**, 1 (1929)

The plate to be tested was cut into six parts, giving the four pieces necessary for one experiment, the two end strips being discarded. The first one was exposed to the sector spectrum without any treatment, next, the second piece was given the same exposure and then it and the third piece were given the fogging exposure simultaneously in a dark room, the latter being then exposed to the sector spectrum. The fourth piece was exposed only to the sector spectrum. Thus the third plate was given the auxiliary exposure before its main exposure, while in the second, this order was reversed. Thus the fog densities of these two plates were made to be equal, as the foggihg exposure given to the two plates was the same.

Results of the Experiments

Two characteristic curves of previously fogged plates are shown in fig. 1, I, II and III, the latter corrected for the fog density, while the former is

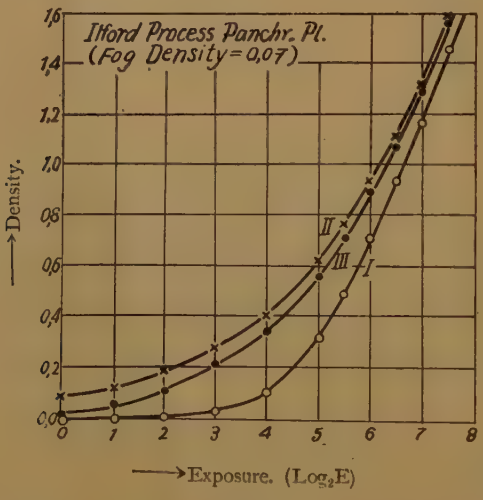


Fig. 1

Effect of previous fogging on a characteristic curve.
I The characteristic curve of the untreated plate.
II „ „ the treated plate without fog correction.
III „ „ „ corrected for the fog density.

not, I representing the corresponding curve of an untreated plate. As is seen from the figure the increase in density produced by the fogging was always greater than the fog density.

The similar results obtained for several kinds of plates are represented

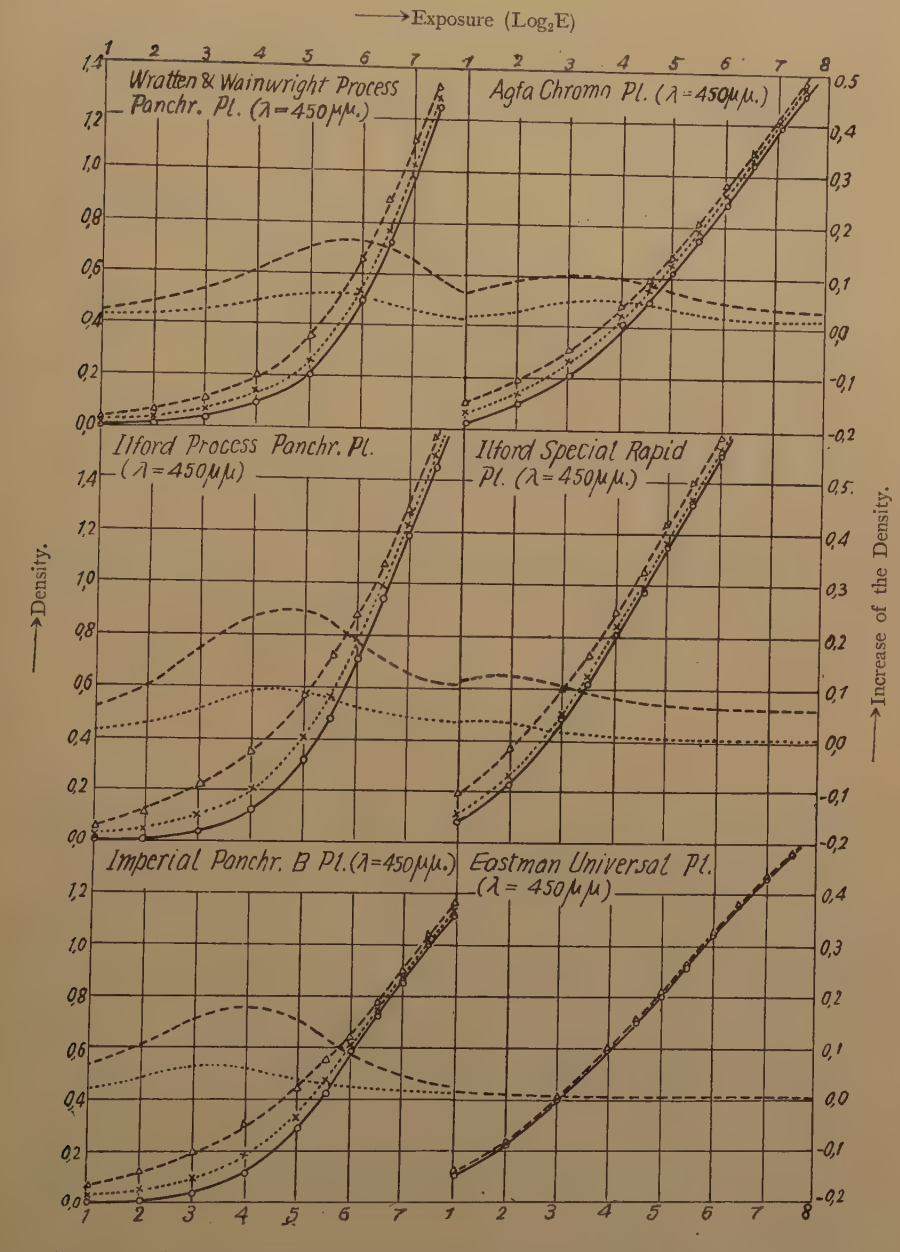

→Exposure (Log₂E)
Wratten & Wainwright Process Panchr. Pl. (λ=450μμ.)
Agfa Chromo Pl. (λ=450μμ.)
Ilford Process Panchr. Pl. (λ=450μμ)
Ilford Special Rapid Pl. (λ=450μμ.)
Imperial Panchr. B Pl. (λ=450μμ.)
Eastman Universal Pl. (λ=450μμ)
→Density.
→Increase of the Density.
→Exposure (Log₂E) —△——△——△—— slighty fogged plates before the exposures.
·····×·····×·····×····· " " " after "
——○——○——○——untreated plates.

Fig. 2

. Comparison of the characteristic curves of the slightly fogged plates with those of the untreated ones.

in fig. 2. The characteristic curves of untreated plates are shown in continuous lines, corresponding curves of previously exposed plates are represented in broken lines, and those of the plates to which the auxiliary exposure were given after the main exposure, in dotted lines. The increase in densities called forth by the fogging at various exposures are also represented with broken and dotted lines. White light was used for fogging throughout these experiments, and corrections for fog density were made according to the formula (8) mentioned above.

The inertia of untreared plates was always the greatest, and that of previously treated ones smallest, and the same is the case with contrast.

It may be said from these results that an auxiliary exposure to a dim light sensitizes a photographic plate in addition to its own blackening action and decreases its contrast, but in the case where the fogging exposure was given after the main exposure this effect is very small. This sensitizing action was marked for all panchromatic plates used in this experiment, but this action was small for a few kinds of orthochromatic and ordinary plates, while this action could not be found in Ilford Process, Imperial Process, Eastman Universal, Wellington Anti-screen plates, etc.

Colour of Fogging Light

Similar experiments were made with coloured lights. For this purpose the rays from the miniature-lamp were filtered through Wratten's monochromatic filters, No. 70 (red), No. 73 (yellow), and No. 76 (violet). The exposure to these fogging lights was adjusted to give equal fog densities for the lights of the three different colours, all these exposures being given before the main exposure.

Fig. 3 shows the effect of slight fogging given by the above mentioned coloured lights on the sensitivity of certain panchromatic plates for rays of various wave lengths, taking the increase of density as ordinate and wave length as abscissa. As the change in the inertia was generally small, the amounts of sensitization at various wave lengths are compared by means of the maximum increase in density. The sensitizing effect of fogging by the red light was always greatest, that by the yellow light medium, and that by the violet light least.

The sensitizing curve shown in Fig. 3 has a somewhat similar form to the sensitivity curve of the plate for each colour, and in each curve the amount of sensitization is great in the spectral regions of red and orange.

Plate I shows the sector spectra taken on the plates, one being un-

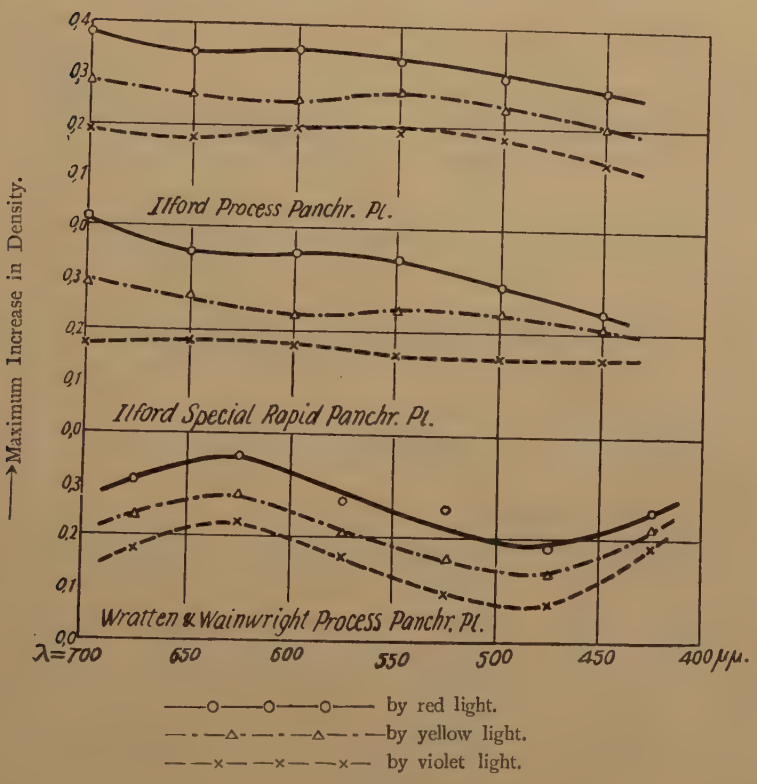


Fig. 3

Sensitizing Action of the Previous Fogging due to Monochromatic Lights.

treated and the other treated with red and violet lights separately. The back-ground of all these photographs is printed to give an equal blackening.

Fatigue of the Sensitizing Action

Fatigue of the sensitizing effect of previous exposure was examined by varying the interval between two exposures. This effect was greatest when the main exposure was made immediately after the fogging exposure, but gradually became smaller when the interval between the two exposures was lengthened. This is seen from figs. 4 and 5, the former representing the characteristic curves and ΔD-logE curves for the plate taken at various intervals after the fogging exposure, and the latter the decay of the maximum increase of density with time. This decay was very small for the first 2 hours, and then it became marked.

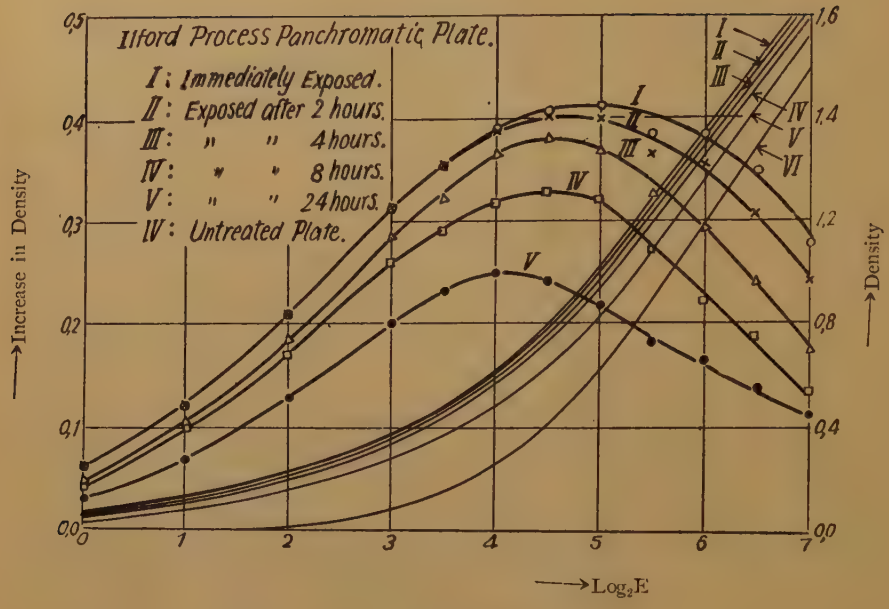


Fig.4

Fatigue of the sensitizing action of previous fogging

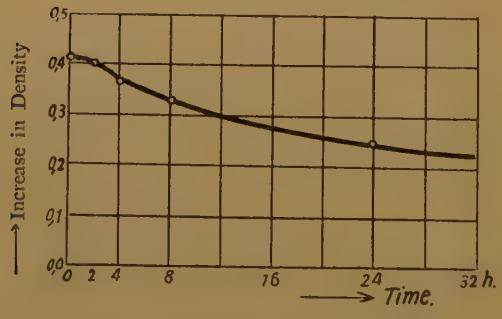


Fig.5

Fatigue of the sensitizing action

Effect of Varying the Fog Density

Next, the relation between the amount of sensitization caused by previous fogging and the fog density was studied. When the time of the fogging exposure is lengthened the fog density becomes greater and the

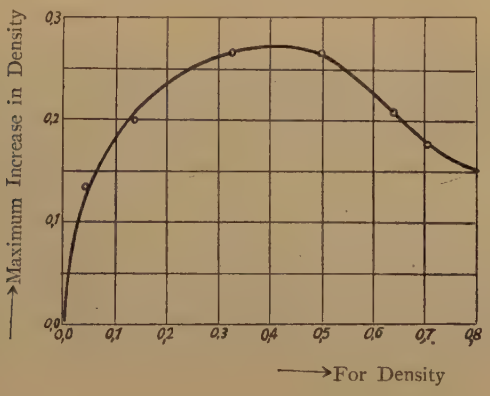


Fig.6

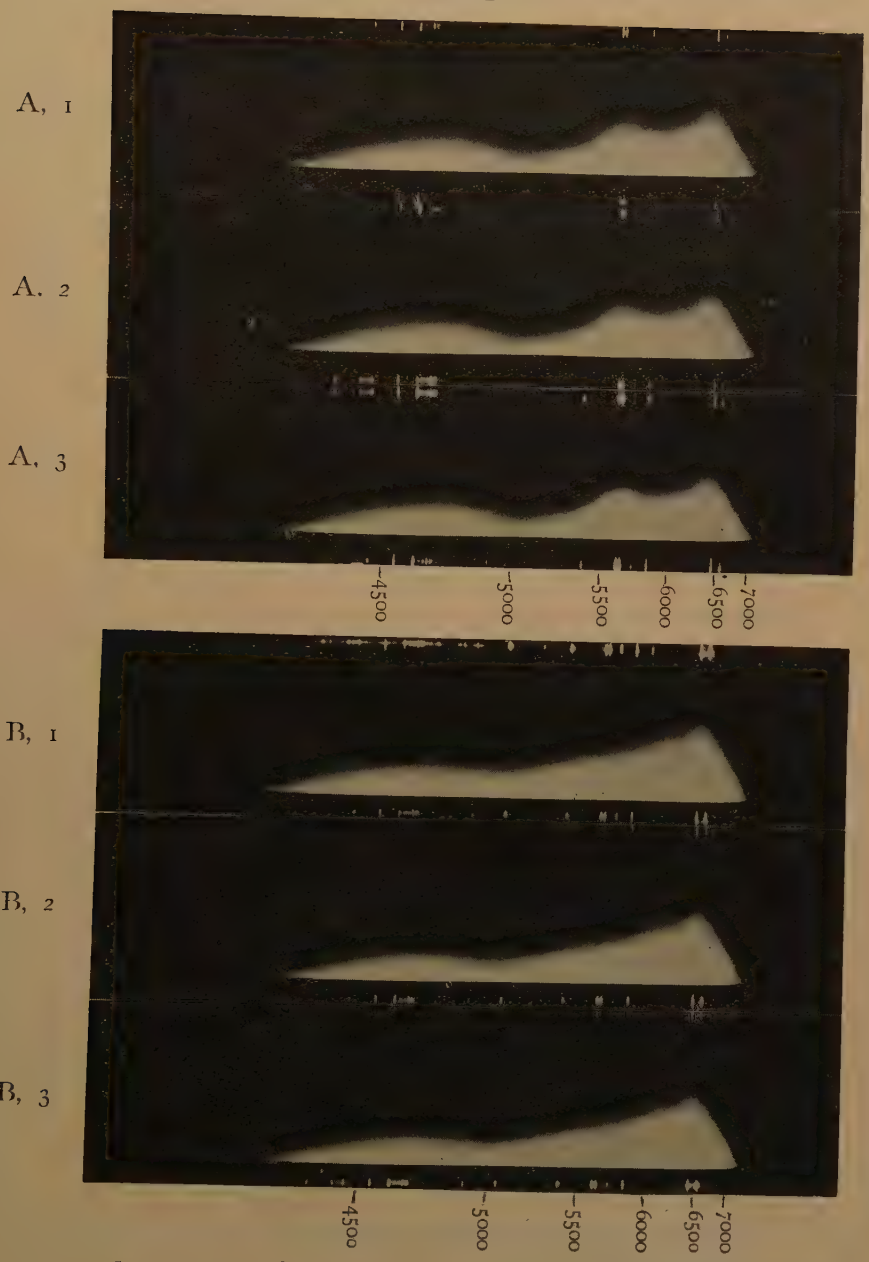
Showing the Relation between the Degree of Sensitizing Action and Fog Density

amount of sensitization is also increased, but it reaches a maximum at a certain density of the fog. This limiting density was about 0.4 for Ilford Special Rapid Panchromatic Plate, but after this was reached, the amount of sensitization was gradually decreased. Fig. 6 represents the relation between the maximum increase in density and the fog density.

It seems to the present writer that the sensitizing effects of a previous fogging is probably caused by the action of optical sensitizers.

In conclusion the author wishes to express his sincere thanks to Prof. M. Kimura for his valuable advice and the great interest he has taken in this investigation, and also to President T. Maruyama of the Konan College for his good offices.

Plate I



1. Sector spectrum taken with a previously fogged plate by red light.
2. " " " " " " " by violet light.
3. " " " with an untreated plate.

A. Wratten & Wainwright Process Panchromatic Plate.
B. Ilford Process Panchromatic Plate.

Studies in Photographic Sensitivity, Part IV.

Desensitizing Action of Previous Fogging by X-Rays

By

Osamu Masaki

(Received February 20, 1929)

Abstract

It was observed by Villard, Wood and others that light destroys an X-ray impression produced on a photographic plate, the amount of this depending much on the nature of the plate. In the present experiments, changes in the shape of the characteristic curves of many commercial photographic plates produced by previous fogging by X-rays were investigated, and the results were as follows. (1) In most commercial plates a fog impression produced by X-rays was not reversed dy light, but the inertia of the plates was increased by a previous exposure to X-rays. (2) The decrease in sensitivity was greater when plates were fogged before the main exposure than when they were fogged after it. (3) The sensitivity of a plate to lights of various wave lengths was decreased by an equal amount by a previous fogging by X-rays. (4) This action of X-rays remained almost the same whatever the time interval between the previous fogging and the main exposure. (5) The change in sensitivity was great for very rapid plates, but the change in contrast was generally small for all plates. (6) The decrease in the sensitivity of a plate produced by X-ray fogging was restored by a second fogging by light, and the sensitivity of a plate gained by previous exposure to a dim light (see the writer's last paper) was also restored by a slight exposure to X-rays. From these facts it was considered that the fogging by X-rays and that by light act independently of each other.

Introduction

Villard[1] found that photographic impressions produced by X-rays in certain plates i.e. Jougla green label, were almost suppressed by exposing to

1 C. R., **128**, 237 (1899)

light. Wood[1] and others also observed that a photographic image produced by X-rays can be reversed by light. But these phenomena depend much on the nature of the plates, as shown by many observers; in most commercial plates, the X-ray impression was not entirely destroyed by light, that is, the density in the part exposed to both X-rays and light was always greater than that in the part exposed only to X-rays, but was always smaller than that exposed only to light. As it seems to the present writer that this is due to a desensitizing effect of X-rays on photographic plates, the following experiments were carried out in order to examine the change produced in the forms of these characteristic curves by exposing slightly to X-ray.

Method of the Experiment

As the source of X-rays, a Coolidge tube with a molybdenum anticathode excited by a 60,000 volt transformer was used.

Four pieces were cut out from a photographic plate; the first one was

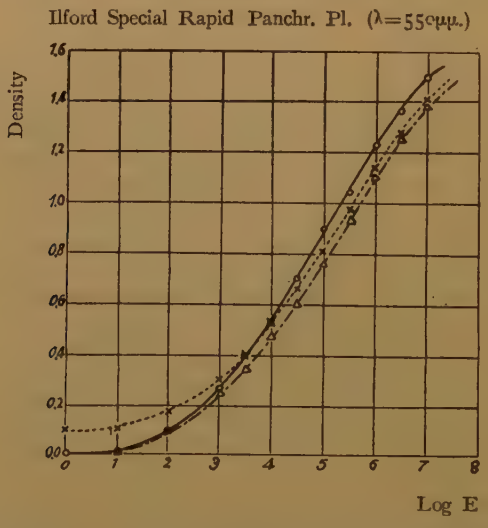


Fig. 1

Desensitizing Action of Previous Fogging by X-Rays

1 Astro. Phys. J., **17**, 361 (1903)

exposed to a sector spectrum as described in the previous paper, the second piece was first exposed to the sector spectrum, and then, this and the third piece were slightly fogged simultaneously by exposing them to X-rays for 5 seconds, the latter being exposed then to the sector spectrum. The last piece was exposed only to the sector spectrum. The densities thus obtained were measured at several spectral regions by a Moll's microphotometer.

A correction for a change in sensitivity due to fatigue of the battery was applied, when a difference between the densities of the first and the fourth piece was detected, and the fog correction was also applied by the method described in the last paper. The characteristic curves of each plate were drawn for lights of certain wave lengths from the measured densities.

The Result

The desensitizing action of a previous fogging by X-rays is easily understood from the curves given in fig. 1, the characteristic curve of an untreated plate being shown with a full line, that of the treated one with a dotted line. The curve represented with a broken line was obtained by applying the correction for the fog to the density of the latter at each exposure. As is seen from the curves, the fog due to X-rays is not reversed by light. If the light destroyed the fog produced by X-rays, the characteristic curve of the treated plate should once descend below the fog density with an increasing exposure, but there is no such tendency. But the density of the treated plate at a higher exposure is always smaller than that of the untreated one, that is, the inertia of the treated plate is increased by this treatment.

The characteristic curves of untreated plates and those of treated plates, one treated before the main exposure and the other after it, were taken with plates of various kinds, and they are given in fig. 2. The correction for the fog density was applied to the measured density at each exposure for all treated plates.

In all plates, the inertia of the plate was increased without exception by the previous fogging with X-rays, this change in inertia being especially marked for high speed plates, but in the case where the auxiliary exposure to X-rays was given after the main exposure, this increase in inertia was small. The change in the contrast was generally small, and in many plates the contrast was increased by a small amount, but in certain plates it was found to be decreased. The relation between the increase in density and the exposure is also represented diagrammatically in the same fig. 2.

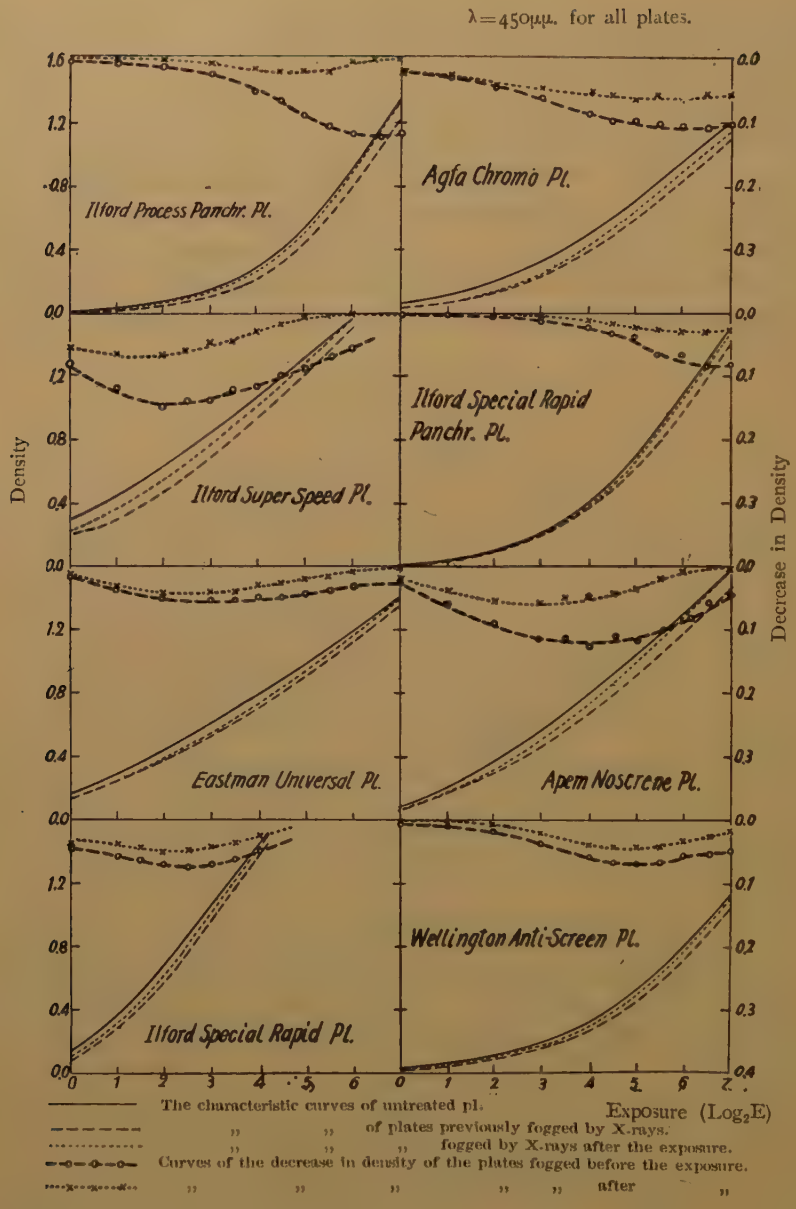

λ=450μμ. for all plates.
Ilford Process Panchr. Pl.
Agfa Chromo Pl.
Ilford Super Speed Pl.
Ilford Special Rapid Panchr. Pl.
Eastman Universal Pl.
Apem Noscrene Pl.
Ilford Special Rapid Pl.
Wellington Anti-Screen Pl.
Density
Decrease in Density
Exposure (Log2E)
The characteristic curves of untreated pl.
" " of plates previously fogged by X-rays.
" " " fogged by X-rays after the exposure.
Curves of the decrease in density of the plates fogged before the exposure.
" " " " " after "

Fig. 2

Effect of Slight Fogging due to X-Rays on the Characteristic Curves

In the following experiments, the amounts of change in sensitivity produced by X-ray fogging were compared by comparing the maximum decrease in density instead of $\triangle$ log i, because the variation in the inertia was generally small, and runs generally parallel to the maximum decrease in density.

Effect of Fogging by X-Rays on the Sensitivity of Plates to Lights of Various Wave Lengths

The influence of previous fogging by X-rays on the sensitivity of plates to lights of various wave lengths was examined with several kinds of plates. The decreases in sensitivity measured at different parts of the sector spectrum were found to be equal to each other within the limits of experimental error. Fig. 3 shows the relation between the maximum decrease

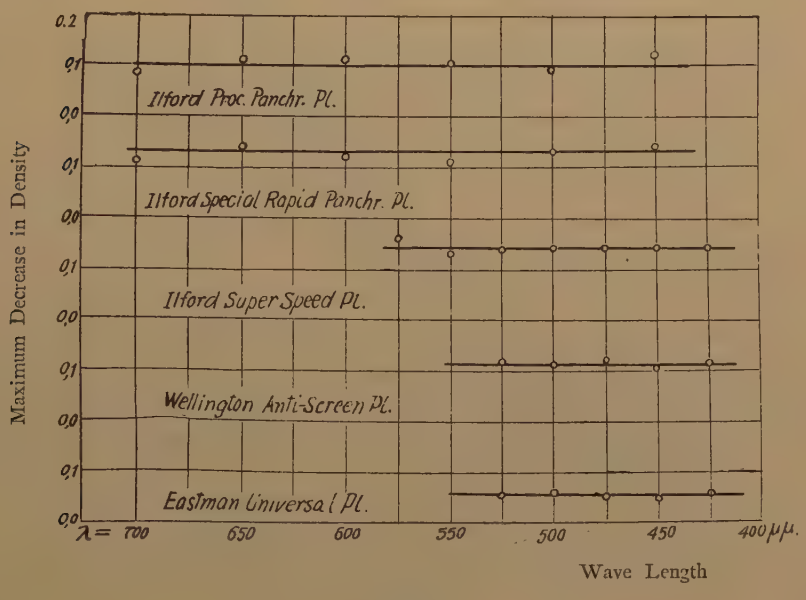


Fig. 3

Effects of Previous Fogging by X-Rays with Lights of Various Wave-Lengths

in density and the wave lengths of the light used for the exposure. From this result, it may be concluded that X-rays desensitize plate equally for all the spectral regions examined.

Variation in Fog Density

Next, the influence of the length of the exposure to X-rays on the desensitizing action of the rays was investigated. The greater the density due to X-ray fogging the larger became both the inertia and contrast for Ilford Super Speed Plates. Fig. 4 shows the characteristic curves for plates previously exposed to X-rays for various times and also shows the variation in the decrease of density with exposures.

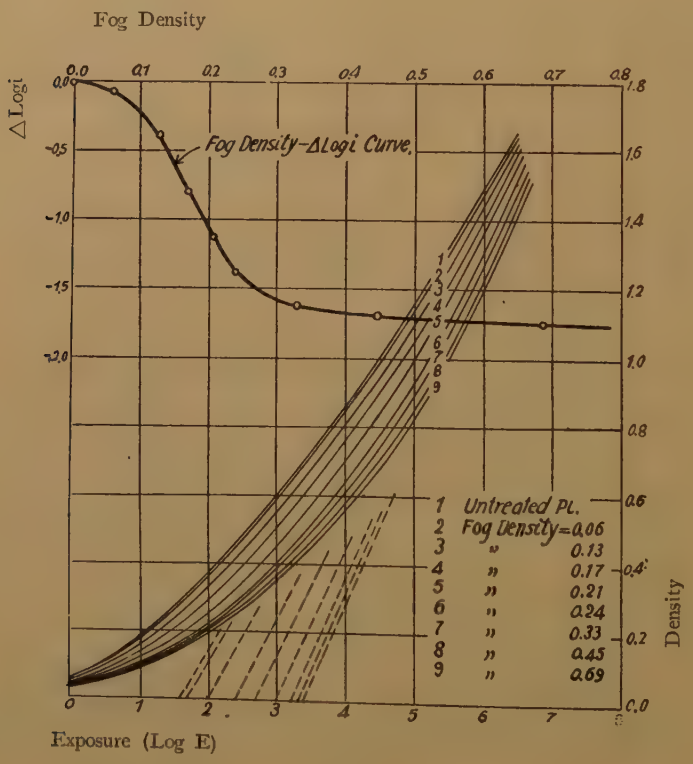


Fig.4

Showing the Effect of Previous Fogging due to X-Rays with Fogging Exposures of Various Lengths

Plate I also represents the sector spectra taken with plates exposed previously to X-rays for various times, the back ground of each plate being printed to give an equal blackening. It can be easily seen from the photo-

graphs that the sensitivity of plates previously exposed to X-rays becomes gradually smaller with increasing time of exposure to the X-rays.

Life of the Desensitized Plate

A number of pieces cut out from a large photographic plate were slightly fogged by X-rays, and were exposed separately to the sector spectrum, at various periods after the previous fogging. As is seen in fig. 5, the amounts of desensitizing action were found to be almost equal within

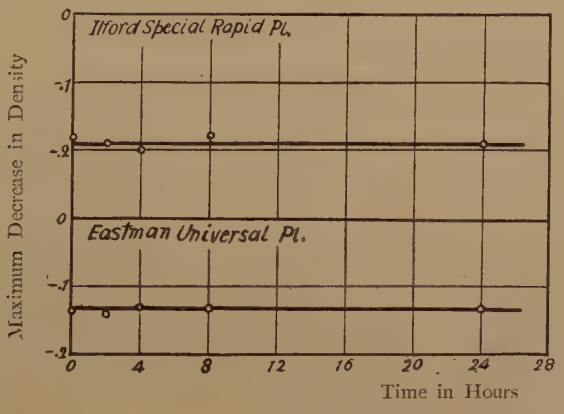


Fig.5

Life of Plates Desensitized by X-Rays

the limits of experimental error. Thus it may be considered that the desensitizing action of X-ray fogging does not decay, but is permanent.

This fact also indicates that the action is quite different from that of light fogging, the latter being temporary, as shown in the last paper of the writer.[1]

Combined Effect of Preliminary Exposures to X-Rays and to Light

It was observed in a preceding experiment[2] that a previous slight fogging by light increases the sensitivity of certain photographic plates more than that given by the law of fogging, and that in the present experiment a similar treatment by X-rays decreases it. Thus it will be interesting to

1, 2 These Memoirs, **12**, 111 (1929)

examine how previous foggings by light and X-rays act on a photographic plate.

Five pieces were cut out from a photographic plate; the first piece was exposed to the sector spectrum without any treatment, the second and the third pieces were exposed to a dim light simultaneously, the former being then exposed to the sector spectrum, while the latter was again exposed to the X-rays for a short time together with the fourth piece. After this treatment, the third, fourth and fifth pieces were exposed to the sector spectrum.

The characteristic curves and △D-logE diagram for the three fogged plates are shown in fig. 6, A, L representing the curve obtained for the plate fogged by light only, X by X-rays only, and L & X by both. Fig. 6, B represents also similar curves in the case where the order of the two previous exposures was reversed. All these curves were taken with Ilford

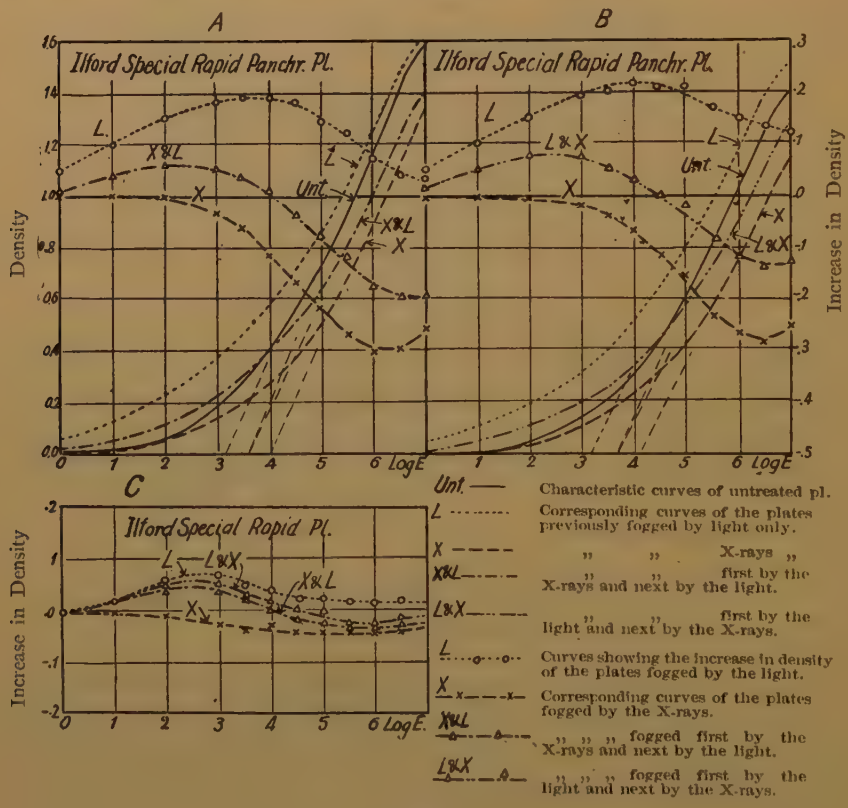

A
B
C
Ilford Special Rapid Panchr. Pl.
Ilford Special Rapid Pl.
Density
Increase in Density
log E
Unt.
L
X
X&L
L&X
Characteristic curves of untreated pl.
Corresponding curves of the plates previously fogged by light only.
" " X-rays "
" " first by the X-rays and next by the light.
" " first by the light and next by the X-rays.
Curves showing the increase in density of the plates fogged by the light.
Corresponding curves of the plates fogged by the X-rays.
" " " fogged first by the X-rays and next by the light.
" " " fogged first by the light and next by the X-rays.

Fig. 6

Effects of Double Foggings by Light and X-Rays

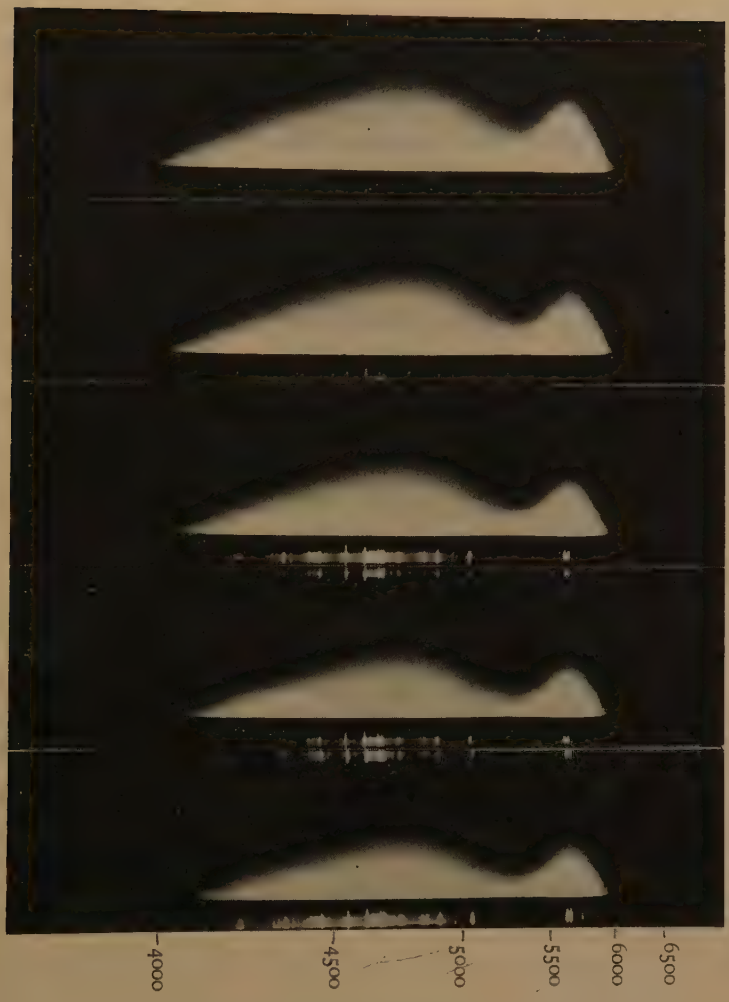
Special Rapid Panchromatic Plates. The curves shown in fig. 6, C are taken with Ilford Special Rapid Plates.

The $\triangle$D-logE curves for the plates fogged by X-rays before and after the light fogging were found to be quite similar, and the increase in density for the plate fogged by X-rays and light is approximately equal to the sum of the corresponding increases of density obtained by fogging due to X-rays and light separately.

From these results it may concluded that the sensitizing action of light and the desensitizing action of X-ray fogging act independently of each other, thus giving the effect equal to their algebraic sum.

In conclusion, the author's sincere thanks are due to Prof. M. Kimura for his kind guidance and the great interest he has taken in this investigation and also to President T. Maruyama of the Konan college for his kind offices.

Plate I



1. Sector spectrum taken with an untreated plate.
2. „ „ taken with a fogged plate by X-rays for 2 seconds.
3. „ „ „ „ „ „ „ for 4 seconds.
4. „ „ „ „ „ „ „ for 6 seconds.
5. „ „ „ „ „ „ „ for 8 seconds.

(Plate: Ilford Super Speed Plate.)

Studies in Photographic Sensitivity, Part V.

Effects of Heat on the Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action

By

Osamu Masaki

(Received February 20, 1929)

Abstract

The present experiments were carried out to examine the effect of heat on the absorption spectrum and photoelectric conductivity of silver bromide, and also to find their relation to the photographic action. The following were the results:– (1) The red end of the absorption spectrum was displaced to the red side by the raising of the temperature of the sample, and those of other silver halides behaved in a similar way. (2) The maximum point in the photoelectric conductivity curve of silver bromide was also displaced towards the same side on its temperature being raised.

Thus heat affects the absorption and photoelectric conductivity of silver bromide in the similar way as it affects the photographic action, indicating that there is some close connection between these three phenomena. This seems to support the photoelectric conductivity theory of photographic action.

Introduction

In a course of the present investigation the writer noticed[1] that the sensitivity of certain photographic plates (i.e. panchromatic, and ordinary slow plates) was increased by the raising of their temperature, but that of ordinary and isochromatic plates of high speed emulsion was decreased by the same treatment, and that in all cases the maximum point of the sensitivity curve was shifted towards the longer wave length side of the

1 These Memoirs; **12**, 1 (1929)

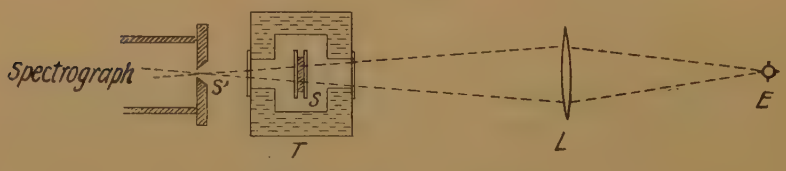
spectrum. The amount of this shift was about 0.8 Å per degree of temperature. The present experiments were carried out to study the effects of heat on the absorption spectrum of silver bromide and also on its photoelectric conductivity, and to see whether or not there is any connection between photographic action, absorption, and photoelectric conductivity of silver bromide.

Effect of Heat on Absorption Spectra of Silver Halides

A small amount of silver bromide was melted on a thin glass plate by holding it over the flame of an alcohol lamp, and a thin film of it was made by squeezing it between this and another glass plate. The thin film of silver bromide thus prepared was placed in a thermostat, and this was placed before the slit of a grating spectrograph as shown in Fig. 1.

Fig. 1

Apparatus to take the absorption spectrum of silver-halide.



E: light source *L*: lens
T: thermostat *S'*: slit
S: thin film of silver halide

This thermostat has double walls, the space between them being filled with water, its temperature being controlled by means of an autoregulator within $\pm 0.5^{\circ}$C. The temperature inside the thermostat can be raised to a required one by means of an electric heater which was placed outside the thermostat.

A 250-watt tungsten lamp with a condensed filament was used as the source of a continuous spectrum. Two spectra, one of which was filtered through the thin film of silver bromide, at a certain temperature, the other being unfiltered, were photographed on one plate, with a spectrum of tin for comparison.

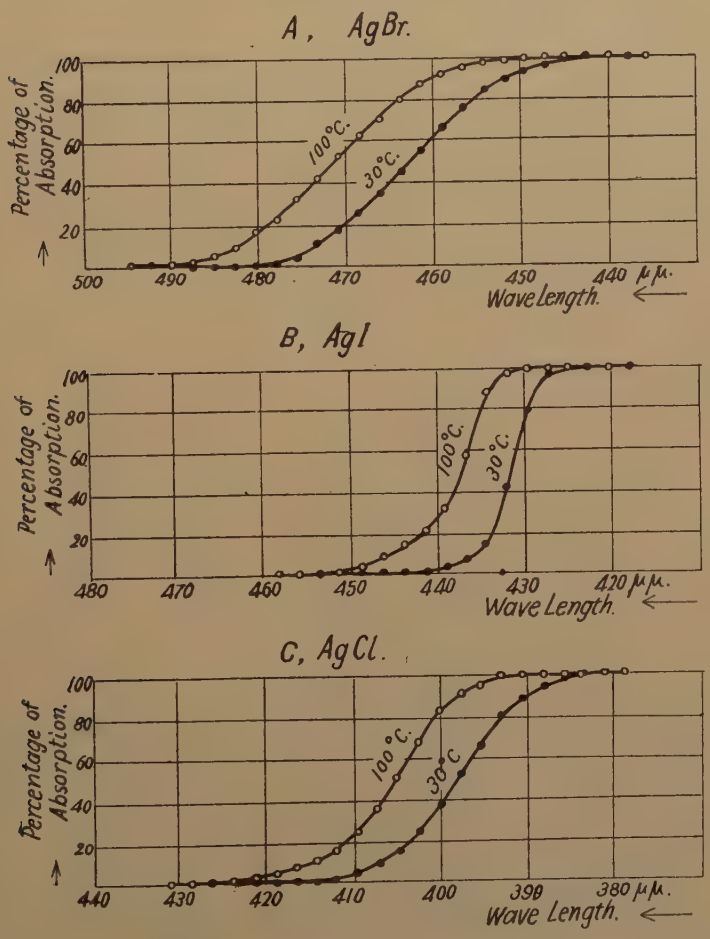
The density of the negative photographic plate was measured by means of a microphotometer with a photoelectric cell, the photoelectric current being once amplified by a triodbulb, and this was measured by a Leads and Northrup's No. 2500-*B* galvanometer, according to the method

devised by Toy, Edgerton and Vick.[1]

The result was as illustrated in Fig. 2, *A*. Fig. 2, *B* and *C* represent similar curves taken with silver iodide and chloride.

Fig. 2

Absorption spectra of silver halides.



The ordinates of the curves represent the percentage of the absorption due to silver halides calculated in the following way.

The intensity of the light at a certain wave length is given by

$$I_0 = k \log \frac{D_\infty}{D_\infty - D_0}$$

1 Phil. Mag.; **6**, 324 (1928)

for the light when unfiltered, and by

$$I = k \log \frac{D_\infty}{D_\infty - D}$$

for the light filtered by silver halide, where D_0 and D represent the densities of the negative plates taken with direct and filtered lights at that spectral region, and D the maximum density of that plate. Therefore, the percentage of the absorption is given by

$$\frac{I_0 - I}{I_0} \times 100 = \left\{ 1 - \frac{\log D_\infty - \log(D_\infty - D)}{\log D_\infty - \log(D_\infty - D_0)} \right\} \times 100.$$

The absorption of a thin film of silver bromide commences at about λ 4900 Å and continues to the ultra-violet region. The longer wave length end of the absorption spectrum was thus shifted to the red side by the raising of its temperature. A shift of about 80 Å was found when the temperature was raised from 30° to 100°C, which is equivalent to 1.1 Å per degree.

Similar amounts of shift were found for silver iodide and silver chloride.

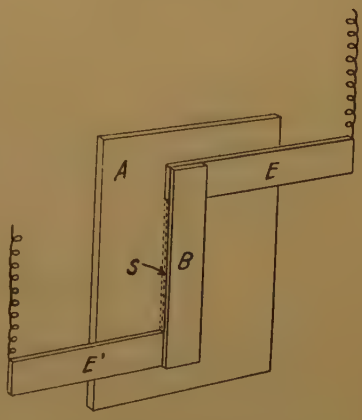
Photoelectric Conductivity of Silver Bromide

Coblentz[1] found that the photoelectric conductivity of silver bromide commences at about λ 5000 Å and becomes sharp maximum at about λ 4650 Å. The present writer investigated the change in the position of the maximum of the photoelectric conductivity curve of silver bromide when the temperature of the sample is varied.

The method of the experiment was similar to that used by Coblentz, with a slight modification as described below.

The sample to be tested was first melted upon a glass or quartz plate, and then the molten material was squeezed by another strip of glass or quartz having a size of about 2×25 mm^2. The electrodes

Fig. 3
Sample



A, *B*: glass or quartz plate.
E, *E'*: silver electrodes.
S: thin film of silver bromide.

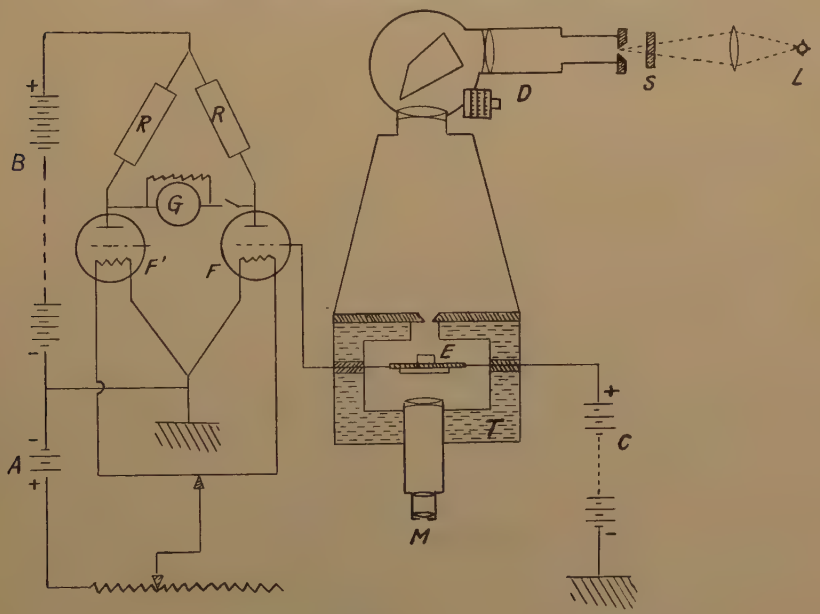
1 Bereau of Standards, Sci. Paper; No. 456. (1922)

consisted of pieces of silver plates of the thickness of about 0.3 mm., placed between two plates as shown in Fig. 3, the thickness of the film being thus made the same as that of the silver electrodes. The distance between the electrodes was about 15 mm. This sample was placed in the same thermostat as that described above. This thermostat was placed just behind a monochromator reconstructed from a Hilger's constant deviation spectrograph, the width of the slit in the focal plane being 1 mm., and the sample to be tested was placed to face the slit at a distance of about 1 cm. from it. One of the electrodes was connected to the anode of a 48 volt battery, the cathode of which was earthed, and the other electrode connected to the grid of an amplifying triodbulb.

An increase in the electric current produced by the illumination was measured by the method devised by Wynn Williams[1], the connection circuit

Fig.4

Apparatus for the measurement of photoelectric conductivity.



L :	1000 watt tungsten lamp.	*A* :	4 volt battery.
S :	shutter.	*B* :	75 volt battery.
D :	constant deviation monochromator.	*C* :	48 volt battery.
E :	thin film of silver bromide.	*F* :	amplifying bulb.
F' :	compensating bulb.	*T* :	thermostat with an autoregulator.
R :	adjustable resistance.		
M :	microscope to test the condition of illumination.		

1 Phil. Mag.; **6**, 324 (1928)

for the measurement being shown in Fig. 4.

Telefunken's *R. E.* 78 bulbs were used as amplifiers, and Leads and Northrup's No. 2500–*B* galvanometer was used for the measurement of currents. The system was initially adjusted so as to give no deflection of the galvanometer when the sample was not illuminated, and the deflections produced by opening the shutter for 5 seconds were recorded for various wave lengths. Other precautions given by Coblentz and Williams were followed in this experiment.

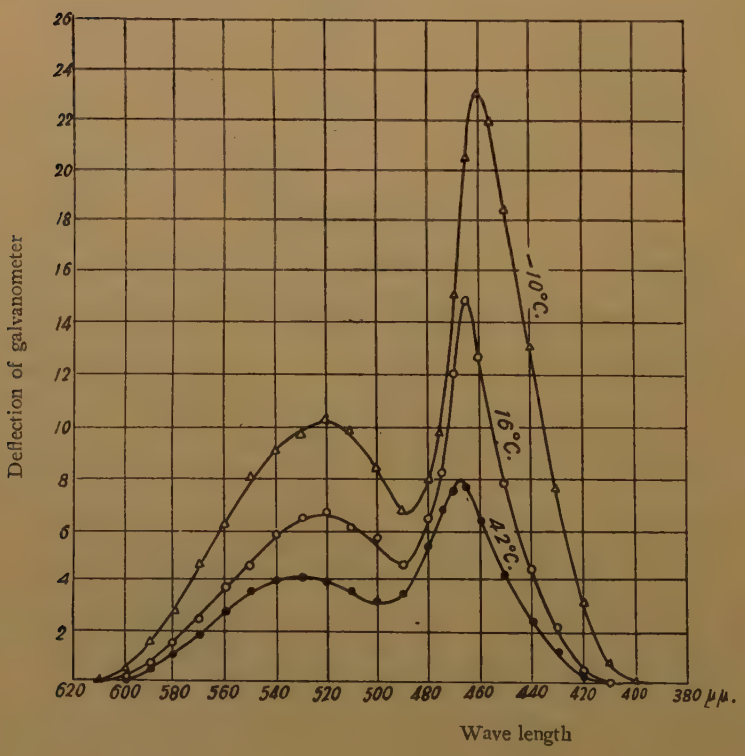
The photoelectric conductivity produced by the illumination became very small and unstable when the sample was heated above 50°C, so that the measurements were made at 42°C, 16°C and −10°C, the last one being obtained by cooling the thermostat with a freezing mixture of ice and common salt.

The curves given in Fig. 5 show the mean of 8 observations taken at three temperatures.

The photoelectric conductivity curve of silver bromide obtained by the

Fig.5

Photoelectric conductivity curve of silver bromide.



present writer has two maxima. The maximum at about λ 4600 Å coincides with that found by Coblentz, indicating that this is due to pure silver bromide, but the other was not found by Coblentz. A further experiment is required to determine the origin of this second maximum.

Generally, the photoelectric conductivity of silver bromide was decreased by the raising of its temperature, and the maximum point of the photoelectric conductivity curve always shifted towards the longer wave length side of the spectrum. The amount of this shift was about 75 Å for a rise of 52°C i.e. about 1.4 Å per degree.

The Relation between the Photoelectric Conductivity and the Photographic Action

In the first part of these studies[1], it was found that the maximum points of the sensitivity curve of a photographic plate was shifted towards the longer wave length side by heating, and that the sensitivity of high speed plates was decreased, but that of panchromatic and slow plates was increased by the same treatment. It was also found that the sensitivity of panchromatic and slow plates was increased by drying, but that of high speed emulsion remained almost the same, the maxima of the sensitivity curves in both cases remaining unchanged by the same treatment.

Comparing these two effects, it may be considered that the sensitizing effect of heat on slow plates may perhaps be due to extreme drying of the plate, but the desensitizing effect of heat on rapid plates and the shifting of the maxima for all plates can not be understood as due to the same reason. From these facts we considered that the decrease in sensitivity and the shift of the maximum points in the sensitivity curve, as is seen for such plates as Apem Non Screened, Ilford Special Rapid, and Eastman Universal plates, must be considered to be really due to the effects of heat. (See Fig. 5; *C*, *D* and *E* in Part 1 of these studies)

Generally, the amounts of this shift for many plates were found to be about 50 Å for a rise of 65°C i.e. 0.8 Å per degree.

In the present experiments it was found that the red ends of the absorption spectra of silver halides shifted towards the red side when their temperature was raised, and that the photoelectric conductivity of silver bromide was decreased and that the maximum of the photoelectric conductivity curve was shifted towards the same side by the same procedure.

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1 These Memoirs; **12**, 1 (1926)

The amount of this shift in the former case was about 1.1 Å. per degree, and that in the latter case was about 1.4 Å per degree.

Thus, it may be osberved that there is a close connection between photographic action, absorption and photoelectric conductivity, as indicated by the similar effects produced by heat on these three phenomena.

This supports the photoelectric conductivity theory of photographic action.

In conclusion, the writer wishes to express his sincere thanks to Prof. M. Kimura, under whose guidance the present experiments were carried out.

Quantitative Analysis of Phosphoric Acid, Part IV.

Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate

By

Masayoshi Ishibashi

(Received February 23, 1929)

Since L. Sonneschein[1] proposed that the precipitation of phosphoric acid as ammonium phosphomolybdate might be utilized for analysis of the acid, a great many works dealing with this subject have been published by several authors. F. Hundeshagen[2] assigned the formula $12MoO_3 . PO_4(NH_4)_3 . 2HNO_3 . H_2O$ or $12MoO_3 . PO_4(NH_4)_3 . 2HCl . H_2O$ to the yellow precipitate of ammonium phosphomolybdate which, when heated to a constant weight at 150° or at 160°–180°[3], was regarded as taking the composition[4], $12MoO_3 . PO_4(NH_4)_3$.

Now if the yellow precipitate of ammonium phosphomolybdate changes quantitatively into $(NH_4)_3PO_4 . 12MoO_3$ the amount of P_2O_5 might be calculated from the weight of it by multiplying by the factor 0.0378. Practically, however, various different factors have been used by different authors, thus

0.0303 (L. Sonneschein)[1]
0.0390 (C. Rammelsberg)[5]

1 J. prak. Chem., (I), **53**, 339 (1851)

2 Zs. anal. Chem., **28**, 141 (1889)

3 R. Finkener: Ber. D. chem. Ges., **11**, 1640 (1878)

4 Accordiug to R. Woy {Chem. Ztg., **21**, 442 (1897)} when ammonium phosphomolybdate contained in a Gooch crucible is put in a large nickel crucible and heated till the bottom of the external crucible becomes dark red it may be weighed as having the composition $P_2O_5.24MoO_3$.

5 Ber. D. chem. Ges., **10**, 1776 (1877)

0.0366 (W. Gibbs)[1]
0.03794 (R. Finkener)[3] (P.91)
0.03753 (F. Hundeshagen)[2]
0.0376 (T.S. Gladding)[3]

This clearly shows that quantitative transformation of phosphoric acid into pure ammonium phosphomolybdate of the formula $(NH_4)_3PO_4 \cdot 12MoO_3$ is very difficult and consequently the application of the reaction to the determination of phosphoric acid can not be expected to give satisfactory results. For this reason, precipitation of phosphoric acid as ammonium phosphomolybdate is generally used only as a means of separating phosphoric acid from other substances, and in order to make a quantitative estimation the phosphomolybdate is dissolved in ammonia water, and from this solution phosphoric acid is precipitated as magnesium ammonium phosphate and weighed as magnesium pyrophosphate. This very tedious process would, however, be greatly simplified, if we could find out the condition under which ammonium phosphomolybdate of a definite composition is precipitated unaccompanied by any impurities and also the temperature at which it takes a definite form suitable for weighing. Moreover, for the determination of a minute quantity of phosphoric acid the phosphomolybdate method will be found far more suitable than the magnesium pyrophosphate method, because the percentage of phosphoric acid in $(NH_4)_3PO_4 \cdot 12MoO_3$ is only 3.78 while that in $Mg_2P_2O_7$ is about 17 times greater, that is, 63.79. The present work was undertaken in the hope of finding such a condition and after several experiments it was confirmed that quite satisfactory results can be obtained in the following way: Ammonium phosphomolybdate is precipitated from a nitric acid solution containing some excess of ammonium nitrate at a high temperature, and the precipitate is filtered with a quartz filter crucible and washed with 2% nitric acid. When it has been thoroughly washed, a filter crucible is placed in a large porcelain crucible and heated gradually first for ten minutes and then strongly at 250°–300° for about thirty minutes. The crucible is then cooled in a desiccator over freshly prepared fused calcium chloride or phosphorus pentoxide. The amount of P_2O_5 is simply obtained from the weight of ammonium phosphomolybdate by multiplying by the theoretical factor 0.0378.

To ascertain how amounts of ammonium molybdate and ammonium

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1 Chem. News, **45**, 31 (1882)
2 Zs. anal. Chem., **32**, 144 (1893)
3 J. Amer. Chem. Soc., **18**, 23 (1896)

nitrate effect the precipitation of ammonium phosphomolybdate and how acidity of the solution and temperature influence the accuracy of the analysis several experiments, described below, were carried out.

Experimental

I. Gravimetric Method

In all the experiments ammonium phosphate, ammonium molybdate, ammonium nitrate and nitric acid were taken as the solution prepared in the following way :

1. Ammonium phosphate solution was prepared by dissolving 1.000 gram of Kahlbaum's ammonium phosphate "Zur Analyse mit Garantieshein" to one litre.
2. Thirty five grams of pure ammonium molybdate $(NH_4)_6MoO_7O_{21}.4H_2O$ obtained from Merck were dissolved to one litre. One ml of such a solution corresponds to 0.001 gram of P_2O_5.
3. Ammonium nitrate solution was prepared by dissolving 400.3 grams of ammonium nitrate to one litre (5 normal).
4. Nitric acid solutions of 5 normal and 0.4 normal (2%).

Table I

No.	Temperature	Time of heating	$(NH_4)_3PO_4.12MoO_3$	P_2O_5 (53.77%)	Diffce
		min.	grm.	%	%
1	40°—45°	10	0.3553	53.72	−0.05
2	40°—45°	10	0.3553	53.72	−0.05
3	50°—55°	5	0.3558	53.79	+0.02
4	50°—55°	5	0.3557	53.78	+0.01
5	60°—63°	5	0.3560	53.83	+0.06
6	60°—63°	5	0.3559	53.81	+0.04
7	70°—73°	5	0.3565	53.90	+0.13
8	70°—73°	5	0.3570	53.97	+0.20
9	70°—73°	30	0.3652	55.22	+1.45
10	boiling	5	0.3609	54.57	+0.80
11	boiling	5	0.3621	54.75	+0.98

1. *Influence of Temperature on the Precipitation of Ammonium Phosphomolybdate*

In each experiment here described, ammonium phosphate was precipitated in the following manner : 25 ml of ammonium phosphate solution were diluted with 100 ml of water and to this were added 50 ml of the ammonium nitrate solution and 25 ml of the ammonium molybdate solution. To this mixture 25 ml of 5 normal nitric acid were added at temperatures varying from 45° to 100° and then cooled for 3 hours, when the precipitation of ammonium phosphomolybdate was found completed, no trace of phosphoric acid being left in the filtrate. The results are as summarized in Table I.

From the table it is seen that a rather large positive error always accompanies the value of phosphoric acid when the working temperatures are higher than 70°. This is evidently due to the formation of a hydrated molybdenum trioxide of the formula $MoO_3 2H_2O$.

Table II

No.	5N-HNO_3		Time of standing	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce	Phosphate in filtrate
	ml	Narmality for total volume		grm.	%	%	
1	100	2.5	over night	0.0483	7.30	−46.47	distinct
2	50	1.7	„ „	0.3412	47.56	−6.18	little
3	50	1.7	„ „	0.3499	52.90	−0.87	trace
4	32	1.3	„ „	0.3555	53.75	−0.02	none
5	32	1.3	„ „	0.3553	53.72	−0.05	„
6	25	1.0	„ „	0.3558	53.79	+0.02	„
7	25	1.0	„ „	0.3556	53.77	±0.00	„
8	25	1.0	3 hours	0.3558	53.79	+0.02	„
9	25	1.0	3 hours	0.3555	53.75	−0.02	„
10	15	0.7	over night	0.3561	53.84	+0.07	„
11	15	0.7	„ „	0.3557	53.78	+0.01	„
12	13	0.6	„ „	0.3571	53.98	+0.21	„
13	13	0.6	„ „	0.3567	53.92	+0.15	„
14	10	0.5	„ „	0.3639	55.02	+1.25	„
15	10	0.5	„ „	0.3617	54.69	+0.92	„

2. *Influence of Concentration of Nitric Acid*

For the precipitation of ammonium phosphomolybdate, 25 ml of the ammonium phosphate solution were made to react upon 25 ml of the ammonium molybdate solution in the presence of 50 ml of the ammonium nitrate solution the strength of the nitric acid being varied from 2.5 to 0.5 normal.

From Table II it will be seen that when nitric acid is more concentrated than 1.7 normal, the precipitation of ammonium phosphomolybdate is always incomplete (No. 1—No. 3), while in the solution in which the concentration of the nitric acid is smaller than 0.6 normal the value of phosphoric acid is found to be higher owing to the precipitation of ammonium nitromolybdate $NH_4NO_3.4MoO_3$.[1] According to the present writer's experiments ammonium nitromolybdate is easily formed in a dilute nitric acid solution containing ammonium nitrate and ammonium molybdate as silky needles insoluble in dilute nitric acid of 1—2% concentration, but soluble both in concentrated nitric acid and in pure water.

To learn the influence of dilution, a solution containing ammonium phosphate, ammonium molybdate and ammonium nitrate in the same quantities as in the previous case was diluted with various quantities of water and 25 ml of 5 normal nitric acid were added. The results are shown in Table III.

Table III

No.	Water added	HNO_3	Time of standing	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce	Phosphate in filtrate
	ml	Normality for total volume	hour	grm.	%	%	
1	50	0.7	3	0.3558	53.79	+0.02	none
2	50	0.7	„	0.3559	53.81	+0.04	„
3	100	0.6	„	0.3562	53.86	+0.09	„
4	100	0.6	„	0.3565	53.90	+0.13	„
5	150	0.5	„	0.3566	53.91	+0.14	„
6	150	0.5	„	0.3570	53.97	+0.20	„
7	200	0.4	„	0.3583	54.17	+0.40	„
8	200	0.4	„	0.3606	54.52	+0.75	„

1 J. Clarens: Zs. anal. Chem., **57**, 463 (1918)
M. S. Posternak: C. R., **170**, 932 (1920)

The positive error due to the formation of ammonium nitromolybdate in a dilute nitric acid solution becomes less when the dilution of the solution is made greater.

From the results shown in Table II and Table III it may be concluded that the most suitable concentration of nitric acid lies between 0.7 and 1.3 normal.

3. *Influence of Amount of Ammonium Nitrate*

For analysis 25 ml of the ammonium phosphate solution with various quantities of ammonium nitrate added were treated with 25 ml of the ammonium molybdate solution the normality of the nitric acid being maintained between 0.7 and 1.3. The results are shown in Table IV.

Table IV

No.	Water	NH_4NO_3 solution		$5N-HNO_3$		Time of standing	$(NH_4)_3PO_4 \cdot 12MoO_3$	P_2O_5	Diffce
	ml	ml	Normality	ml	Normality	hour	grm.	%	%
1	/	5	0.4	10	0.8	3	0.3585	54.20	+0.43
2	/	5	0.4	10	0.8	„	0.3580	54.13	+0.36
3	70	20	0.6	25	0.8	„	0.3557	53.78	+0.01
4	70	20	0.6	25	0.8	„	0.3560	53.83	+0.06
5	/	10	0.7	15	1.0	„	0.3557	53.78	+0.01
6	/	10	0.7	15	1.0	„	0.3560	53.83	+0.06
7	70	50	1.3	25	0.7	„	0.3558	53.79	+0.02
8	70	50	1.3	25	0.7	„	0.3559	53.81	+0.04
9	/	20	1.6	25	1.3	„	0.3560	53.83	+0.06
10	/	20	1.6	25	1.3	„	0.3558	53.79	+0.02
11	/	50	2.0	25	1.0	„	0.3558	53.79	+0.02
12	/	50	2.0	25	1.0	„	0.3556	53.77	±0.00
13	/	75	2.5	30	1.0	„	0.3557	53.78	+0.01
14	/	75	2.5	30	1.0	15	0.3557	53.78	+0.01
15	/	115	2.8	40	1.0	3	0.3545	53.60	−0.17
16	/	115	2.8	40	1.0	15	0.3552	53.71	−0.06
17	/	250	3.3	70	0.9	15	0.3483	52.66	−1.11
18	/	250	3.3	70	0.9	15	0.3495	52.84	−0.93

It is thus seen from the table that the normality of ammonium nitrate must be kept between 0.6 and 2.5.

4. *Influence of Amount of Ammonium Molybdate*

Ammonium phosphomolybdate was precipitated from a solution containing 25 ml of the ammonium phosphate solution and 20 ml of the ammonium nitrate solution and also of 5 normal nitric acid. The total volume of the solution was so adjusted that the concentration of both nitric acid and ammonium nitrate was nearly one normal. The solution containing the precipitate after having been heated for about 5 minutes at 50°–60° was left to cool for 3 hours and filtered. The results of the experiments are shown in the following table.

Table V

No.	Water	Amm. Molybdate		$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce
	ml	ml	Mol. ratio to $(NH_4)_2HPO_4$	grm.	%	%
1	20	15	1.3	0.3541	53.54	−0.23
2	20	15	1.3	0.3549	53.66	−0.11
3	18	17	1.5	0.3557	53.78	+0.01
4	18	17	1.5	0.3555	53.75	−0.02
5	15	20	1.8	0.3556	53.77	±0.00
6	15	20	1.8	0.3559	53.81	+0.04
7	10	25	2.2	0.3558	53.79	+0.02
8	10	25	2.2	0.3557	53.78	+0.01
9	/	35	3.1	0.3560	53.83	+0.06
10	/	35	3.1	0.3560	53.83	+0.06
11	/	40	3.5	0.3567	53.93	+0.16
12	/	40	3.5	0.3566	53.91	+0.14
13	/	50	4.4	0.3596	54.37	+0.60
14	/	50	4.4	0.3606	54.52	+0.75

The above table shows that the molar ratio of ammonium molybdate to ammonium phosphate should be maintained at 1.5—3.0. When less is used, it gives a negative error, when more, a positive.

5. *Suitable Amounts of the Phosphate to be taken for Analysis*

As ammonium phosphomolybdate is 14 times heavier than ammonium phosphate, if we take several decigrams of the latter for analysis of phosphoric acid we have to treat with several grams of ammonium phosphomolybdate. This makes the process very tedious and the result of analysis inaccurate.

To determine what is the most suitable quantity of ammonium phosphate to be taken for analysis several experiments were performed twice as much ammonium molybdate being used as theory requires and the concentration of ammonium nitrate and of nitric acid being always kept at one normal. The precipitate of ammonium phosphomolybdate was heated at 50°—60° for five minutes with the mother liquor and left to stand over night, when the precipitation of phosphoric acid was observed to have taken place completely. The precipitate was ignited at 250°—300° for 20—120 minutes according to its amount. The results are shown thus :——

Table VI

No.	$(NH_4)_2HPO_4$	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce
	grm.	grm.	%	%
1	0.2500	3.7183	56.22	+2.45
2	0.2500	4.3660	66.01	+12.24
3	0.1250	1.7755	53.69	−0.08
4	0.1250	1.7760	53.73	−0.04
5	0.0625	0.8886	53.74	−0.03
6	0.0625	0.8886	53.74	−0.03
7	0.0250	0.3557	53.78	+0.01
8	0.0250	0.3555	53.75	−0.02
9	0.0100	0.1424	53.83	+0.06
10	0.0100	0.1421	53.71	−0.06

The most favourable quantities of ammonium phosphate which are to be taken for analysis were thus found to lie between 0.01 and 0.13 grams $\{(NH_4)_3PO_4.12MoO_3$, 0.14—1.78 grams$\}$. When more ammonium phosphate was taken than this limit, the value of phosphoric acid was found to

be remarkably high (No. 1—No. 2). This is probably due to the formation of ammonium nitromolybdate.

6. *The Best Procedure for Precipitating Ammonium Phosphomolybdate, Composition of Phosphomolybdate and how to Dry it*

From what we have so far learned, the best procedure for precipitating phosphoric acid as ammonium phosphomolybdate may be established as follows :—

To a neutral solution containing 0.006—0.07 grams of P_2O_5, ammonium molybdate is added in an excess (about twice the theoretical quantity). The total volume of the solution should then be about 60 ml. Now 20 ml of 5 molar ammonium nitrate solution and of 5 normal nitric acid are added, whereupon the solution becomes distinctly yellow and begins to precipitate ammonium phosphomolybdate. The solution is then heated to 50°—60° in a water bath for about five minutes with occasional stirring and left to cool for three hours. The precipitate is transferred into a quartz filter crucible and quickly washed with 2% nitric acid[1] under suction till the filtrate ceases to give the reaction of molybdenum. The filter crucible is placed in a large porcelain crucible containing some glass wool, and heated gradually for the first ten minutes and then at 250°—300° till its weight becomes constant. For the precipitate amounting 0.3—0.5 grams ignition for about 30 minutes is quite sufficient. The ignited filter crucible is then cooled in a desiccator containing phosphorus pentoxide or $CaCl_2.1\frac{1}{5}H_2O$ and weighed. The weight of the precipitate multiplied by the theoretical factor 0.0378[2] gives the amount of P_2O_5.

The composition of ammonium phosphomolybdate ignited at a temperature of 250°—300° is $(NH_4)_3PO_4.12MoO_3$. This anhydrous substance is exceedingly hygroscopic and gradually changes into the hydrated form $(NH_4)_3PO_4.12MoO_3.3H_2O$ even in a desiccator containing $CaCl_2.2H_2O$. This

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1 The precipitates of ammonium phosphomolybdate is generally washed with water, ice water, alcohol or 1% nitric acid. With these treatments, however, the precipitate was observed to become partly colloidal and to pass through the filter. It was found safest to wash with 2% nitric acid.

2 Strictly speaking the theoretical factor is 0.03784. But as the thoroughly dried precipitate is very hygroscopic it absorbs some moisture while it is being weighed even though the weighing is done as promptly as possible. Perhaps for this reason the factor 0.0378 gives better results.

hydrated phosphomolybdate is also obtained by thoroughly washing ammonium phosphomolybdate, precipitated from a nitric acid solution, with water or dilute potassium nitrate solution. To prove this, the following experiments were performed :

After washing the yellow precipitate of ammonium phosphomolybdate with water till the filtrate no longer gave the nitric acid reaction, it was dried in the open air for a few days and then placed in a desiccator over $CaCl_2.2H_2O$. When its weight became constant it was ignited at 250°—300° for 30 minutes and cooled in another desiccator containing P_2O_5 or $CaCl_2.1\frac{1}{5}H_2O$. The ratio of its weights after and before ignition was as follows :

After ignition	Before ignition	Ratio	$\frac{(NH_4)_3PO_4.12MoO_3}{(NH_4)_3PO_4.12MoO_3.3H_2O}$
0.2431 grm.	0.2503 grm.	0.9712	0.9720
0.2935 „	0.3020 „	0.9719	„
0.3904 „	0.4012 „	0.9731	„

The dried phosphomolybdate was next dissolved in dilute ammonia water and nearly neutralized with dilute hydrochloric acid and from this solution phosphoric acid was precipitated as magnesium ammonium phosphate according to the writer's method[1] and determined as magnesium pyrophosphate.

$(NH_4)_3PO_4.12MoO_3.3H_2O$	$Mg_2P_2O_7$	P_2O_5	$\frac{P_2O_5 \times 100}{(NH_4)_3PO_4.12MoO_3.3H_2O}$
4.0910 grm.	0.2354 grm.	3.67%	3.68
3.4834 „	0.2001 „	3.67 „	„
3.0812 „	0.1776 „	3.68 „	„

The formula $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ given by A. Neumann[2] and Z. Shibata[3] to ammonium phosphomolybdate thoroughly washed with water seems to be erroneous.

As was stated before, anhydrous ammonium phosphomolybdate is so hygroscopic that it changes into the trihydrate in a desiccator containing $CaCl_2.2H_2O$. Even when it is kept long over $CaCl_2.1.2H_2O$ or concentrated sulphuric acid (1.84) it gradually absorbs moisture and becomes partially hydrated as is shown by the following experiments :

0.1805 grams of anhydrous ammonium phosphomolybdate, when kept for 50 days over $CaCl_2.1.2H_2O$, became 0.1818 grams. This increase in weight shows the formation of hydrate, $(NH_4)_3PO_4.12MoO_3.2.25H_2O$.

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1 These Memoirs, **12**, 23 (1929)

2 Zs. anal. Chem., **42**, 791 (1903)

3 J. Chem. Soc., Japan, **47**, 242 (1926)

0.2826 grams of the trihydrate lost 0.0062 grams after standing for 50 days over concentrated sulphuric acid (1.84). The loss corresponds to 1.03 H_2O, so that the hydrate newly formed is expressed by $(NH_4)_3PO_4.12MoO_3$ $1.97H_2O$.

When exposed in the open air the trihydrate takes up more moisture and the weight is thus increased about 1.27%.

Trihydrate	Weight increase	
grm.	grm.	%
4.0910	0.0520	1.27
3.4834	0.0441	1.27
3.0812	0.0392	1.27

The weight of moisture corresponds to 1.4 molecules of water and therefore the hydrate thus formed may be expressed by $(NH_4)_3PO_4.12MoO_3.4.4H_2O$.

Ammonium phosphomolybdate washed with dilute nitric acid (about 2.5 normal) and kept for 50 days over $CaCl_2.2H_2O$ was also observed to absorb moisture in the open air. The results of experiments carried out to confirm its composition before and after absorption of moisture, were as follows:

a = weight of the molybdate dried over $CaCl_2.2H_2O$

b = the weight after ignition at 250°—300°

c = the weight after keeping ignited molybdate over $CaCl_2.2H_2O$ for 12 hours

a	b	$\frac{b \times 100}{a}$	$\frac{(NH_4)_3PO_4.12MoO_3 \times 100}{(NH_4)_3PO_4.12MoO_3.HNO_3.2H_2O}$
grm.	grm.		
0.2556	0.2426	94.91	94.99
0.2654	0.2520	94.95	,,
0.3421	0.3252	95.06	,,
b	c	$\frac{b \times 100}{c}$	$\frac{(NH_4)_3PO_4.12MoO_3 \times 100}{(NH_4)_3PO_4.12MoO_3.3H_2O}$
grm.	grm.		
0.2426	0.2497	97.16	97.20
0.2520	0.2583	97.56	,,
0.3252	0.3337	97.45	,,

Percentage of phosphoric acid in the molybdate dried over $CaCl_2.2H_2O$ was determined:

Molybdate	$Mg_2P_2O_7$	P_2O_5	$\frac{P_2O_5 \times 100}{2(NH_4)_3PO_4.12MoO_3.HNO_3.2H_2O}$
grm.	grm.	%	

3.9260	0.2210	3.59	3.60
1.9518	0.1095	3.58	,,
2.8413	0.1591	3.57	,,

From the above result there is absolutely no doubt that ammonium phosphomolybdate washed with dilute nitric acid and dried over $CaCl_2.2H_2O$ has the composition represented by the formula $(NH_4)_3PO_3.12MoO_3.HNO_3.2H_2O$. The formula, $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ first given by Hundeshagen[1] and hitherto accepted as true must be corrected.

This phosphomolybdate containing a molecule of nitric acid and two molecules of water has also a tendency to absorb water in the open air. The increase in weight thus produced was found by measurement to amount to 2.79% which nearly corresponds to three molecules of water. The formula of the molybdate after absorbtion of water may therefore be expressed by $(NH_4)_3PO_4.12MoO_3.HNO_3.5H_2O$.

As there are many varieties of ammonium phosphomolybdate differing from each other in the degree of hydration, and some of them take up moisture even in an ordinary desiccator, strict attention should be paid to their dehydration before weighing.

It may be mentioned here that the sensibility of the reaction by which phosphoric acid is precipitated as ammonium phosphomolybdate was examined by treating 0.0001 grams of ammonium phosphate (0.000054 grams of P_2O_5) with 10 ml of the ammonium molybdate solution in a solution containing 10 ml of the ammonium nitrate solution and of 5 normal nitric acid together with 20 ml of water. The yellow precipitate began to appear after 30 minutes and became distinct after an hour. Sensibility is, therefore, expressed by 0.000054 (P_2O_5) : 50 or 1 : 1,000,000. Even with 0.00001 grams of ammonium phosphate (0.0000054 grams of P_2O_5) the precipitate of ammonium phosphomolybdate could still be observed after a night's standing, from which sensibility as small as 1: 10,000,000 is deduced.

7. *Influence of Various Substances on the Precipitation of Ammonium Phosphomolybdate*

In order to see the influence of various acids and salts on the precipitation of ammonium phosphomolybdate, 25 ml of the ammonium phosphate solution were treated with 25 ml of the ammonium molybdate solution in the presence of 20 ml of the ammonium nitrate solution and also of 5 normal nitric acid and 10 ml of a solution of the substance to be tested.

1 Loc. cit.

Table VII

No.	Substance mixed		Time of standing	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce	Phosphate in filtrate
	Name	grm.		grm.	%	%	
1	HCl	2.6	over night	0.3493	52.81	−0.96	trace
2	„	1.3	„ „	0.3545	53.20	−0.57	trace
3	„	0.9	„ „	0.3559	53.81	+0.04	none
4	„	0.9	„ „	0.3555	53.75	−0.02	„
5	H_2SO_4	1.9	5 hours	0.3627	54.84	+1.07	„
6	„	0.9	5 hours	0.3582	54.15	+0.38	„
7	CH_3COOH	4.2	over night	0.3555	53.75	−0.02	„
8	„	2.1	„ „	0.3556	53.77	±0.00	„
9	Tartaric acid	1.5	„ „	0.3129	47.31	−6.46	distinct
10	Citric acid	1.5	„ „	0.1405	21.24	−32.53	distinct
11	Oxalic acid	1.0	„ „	no precipitation takes place			
12	$NaNO_3$	3.0	„ „	0.3549	53.66	−0.11	none
13	„	3.0	„ „	0.3550	53.67	−0 10	„
14	KNO_3	3.0	„ „	0.3550	53.67	−0.10	„
15	„	2.0	„ „	0.3553	53.72	−0.05	„
16	$Ca(NO_3)_2$	2.0	„ „	0.3553	53.72	−0.05	„
17	„	1.0	„ „	0.3553	53.72	−0.05	„
18	$FeCl_3$	1.0	„ „	0.3539	53.51	−0.26	trace
19	„	0.3	„ „	0 3547	53.63	−0.14	trace

Hydrochloric acid.—The precipitation of ammonium phosphomolybdate from a solution containing more than I gram of hydrogen chloride in every 100 ml is incomplete (No. 1—No. 2).

This incompleteness can easily be removed by adding ammonium molybdate in large excess. But as this treatment becomes the cause of a positive error (see Table V) the precipitate thus formed must be dissolved and reprecipitated once again.

Sulphuric acid.—This acid becomes a cause of positive error which, however, may be got rid of by double precipitation.

Acetic acid.—No influence.

Tartaric acid and citric acid.—Both these acids have the effect of lowering the value of phosphoric acid, perhaps owing to the formation of some soluble complex molybdate whose complexity is nearly of the same degree as that of the phosphomolybdate. Though this hindrance may be removed by using ammonium molybdate in a large excess another hindrance causing positive error is thus introduced, so that, the precipitate must be redissolved in dilute ammonia and again precipitated.

Oxalic acid.—Not only is the precipitation of ammonium phosphomolybdate entirely obstructed but the precipitate once formed is also dissolved by oxalic acid to no small extent. Perhaps the complexity of the compound[1] formed by molybdic acid and oxalic acid is greater than that of the phosphomolybdate complex. This hindrance may also be removed in a manner similar to that used in the case of tartaric acid.

Sodium nitrate, potassium nitrate and calcium nitrate.—These all show almost no bad influence.

Ferric chloride.—This makes the precipitation of phosphomdlybdate somewhat incomplete. This hindrance may be removed in the same way as in the case of tartaric, citric and oxalic acids.

II. Volumetric Method

The following five methods for volumetrically determining phosphoric acid precipitated as ammonium phosphomolybdate are known :

1. The precipitate is dissolved in a known excess of a standard alkali solution and alkali remaining as excess is titrated with an acid.
2. The precipitate is boiled with a concentrated alkali solution and the amount of ammonia evolved is determined volumetrically.
3. The precipitate is treated with a known quantity of a standard alkali solution and after driving off ammonia the excess of alkali left unchanged is titrated.
4. The dark greenish brown or brown solution obtained by reducing ammonium phosphomolybdate is titrated with potassium permanganate.
5. Iodine liberated from potassium iodide by the action of the molybdate is titrated.

By tracing these methods and comparing the results obtained the

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1 A. Rosenheim: Zs. anorg. Chem., **4**, 352 (1893)
A. Rosenheim u. A. Bertheim: Ibid., **34**, 427 (1903)
R. F. Weinland u. K. Zimmermann: Ibid., **108**, 248 (1919)
F. Feigl: Zs. anal. Chem., **74**, 386 (1928)

present writer found the first method to be the best.

H.Pemberton[1] thought that ammonium phosphomolybdate thoroughly washed with water or ammonium nitrate just reacts with alkali according to the equation given below, and the excess of alkali left unchanged may be exactly titrated with an acid, phenolphtalein being used as indicator.

$2(NH_4)_3PO_4.12MoO_3 + 46NaOH = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O$

If this view is correct 1ml of $\frac{N}{10}$–NaOH used up must correspond to 0.0003089 grams of P_2O_5. The results of the present writer's experiments turned out somewhat different.

Ammonium phosphomolybdate well washed with water and dehydrated over $CaCl_2.2H_2O$ was analysed and the percentage of P_2O_5 {theoretical value calculated for $(NH_4)_3PO_4.12MoO_3.3H_2O$, 3.68%} was calculated.

Amm.phosphomolybdate grm.(=a)	$\frac{N}{10}$–NaOH ml(=b)	P_2O_5 $\%\left(=\frac{b \times 0.0003089 \times 100}{a}\right)$ %	Diffce %
0.1286	15.58	3.74	0.06
0.1167	14.14	3.74	0.06
0.1846	22.39	3.75	0.07
0.2822	34.19	3.74	0.06
0.1464	17.89	3.76	0.08

The value of phosphoric acid is thus found constant but always about 0.06% higher. The main cause of this constant error may be attributed to the fact that the end point indicated by phenolphtalein in the last titration of alkali is not what we really want to determine. For the P_H value of the solution containing diammonium hydrogen phosphate, ammonium molybdate and sodium molybdate exactly in the proportion of $2(NH_4)_2HPO_4$, $(NH_4)_2MoO_4$ and $23Na_2MoO_4$ was found to be 6.8—7.2 while that of the solution in which red phenolphtalein is decolourized is 8.3. Use of other indicators such as neutral red, bromthymol blue, bromcresol purple and cresol red, however, was found less reccommendable, for the end point shown by them was not quite so sharp as to give a constant result. After many trials it was finally found that the method giving the best and most constant result is to use phenolphtalein in the titration of alkali as Pemberton did and to multiply the number of mls of $\frac{N}{10}$–NaOH found by the factor 0.0003030 instead of the theoretical number 0.0003089, as is shown in the experiments described below.

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1 J. Amer. Chem. Soc., **15**, 382 (1893); **16**, 378 (1894)

Experimental

Procedure.—Ammonium phosphomolybdate prepared from a definite quantity of ammonium phosphate according to the manner described in the part dealing with gravimetric method is transferred to a filter by decantation and washed with 1% potassium nitrate solution till the filtrate reacts neutral to litmus paper. The filter containing the precipitate is now put in a beaker into which an excess of $\frac{N}{10}$–NaOH solution is then poured, the beaker being shaken all the time. When the precipitate of ammonium phosphomolybdate is completely dissolved the excess of alkali is titrated with $\frac{N}{10}$–HCl, phenolphtalein being used as indicator. Though the presence of filter paper does not interfere with the accuracy of titration still it will be found convenient to select as small a filter as possible.

Experiment I

Ammonium phosphomolybdate was precipitated from a solution containing 0.0250 grams of ammonium phosphate, 25 ml of the ammonium molybdate solution, 20 ml of the ammonium nitrate solution, 20 ml of 5 normal nitric acid and 35 ml of water. The results of titration are as follows :—

$\frac{N}{10}$ – NaOH	Factor	P_2O_5	Diffce
ml		%	%
44.42	0.0002842	50.50	−3.27
	0.0002960	52.59	−1.18
	0.0003089	54.89	+1.12
	0.0003030	53.84	+0.07
44.36	0.0002842	50.42	−3.35
	0.0002960	52.52	−1.25
	0.0003089	54.81	+1.04
	0.0003030	53.76	−0.01

$\frac{N}{10}$ – NaOH	Factor	P_2O_5	Diffce
44.42	0.0002842	50.50	−3.27
	0.0002960	52.59	−1.18
	0.0003089	54.89	+1.12
	0.0003030	53.84	+0.07
44.45	0.0002842	50.53	−3.24
	0.0002960	52.63	−1.14
	0.0003089	54.92	+1.15
	0.0003030	53.87	+0.10
44.34	0.0002842	50.41	−3.36
	0.0002960	52.50	−1.27
	0.0003089	54.81	+1.04
	0.0003030	53.74	−0.03

If the precipitate of ammonium phosphomolybdate after thorough washing is of the composition $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ or $(NH_4)_3PO_4.12MoO_3.HNO_3.2H_2O$ the factors by which to multiply the number of ml of $\frac{N}{10}$–NaOH must be 0.0002842 and 0.0002960 respectively. The fact that both factors fail to give satisfactory results, as is seen in the table, may be taken as another evidence against such compositions.

Experiment 2

To prepare ammonium phosphomolybdate 0.0100 grams of ammonium phosphate, 10 ml of the ammonium molybdate solution, 10 ml of the ammonium nitrate solution and also of 5 normal nitric acid and 20 ml of water were employed. The results of titration are tabulated thus :

$\frac{N}{10}$ – NaOH	Factor	P_2O_5	Diffce
ml		%	%
17.77	0.0003030	53.84	+0.07

$\frac{N}{10}$—NaOH	Factor	P_2O_5	Diffce
17.75	„	53.78	+0.01
17.75	„	53.78	+0.01
17.77	„	53.84	+0.07

Experiment 3

To learn how far this method is applicable for the determination of a minute quantity of phosphoric acid, ammonium phosphomolybdate prepared from 0.0050 grams of ammonium phosphate was analysed with the following results :—

$\frac{N}{10}$—NaOH	Factor	P_2O_5	Diffce
ml		%	%
8.90	0.0003030	53.93	+0.16
9.85	„	53.63	−0.14
9.85	„	53.63	−0.14
8.88	„	53.81	+0.04

Experiment 4

With the aid of a micro-burette giving readings of 0.0001 ml, ammonium phosphomolybdate formed from 0.0025 grams of ammonium phosphate was analysed.

$\frac{N}{10}$—NaOH	Factor	P_2O_5	Diffce
ml		%	%
4.502	0.0003030	54.56	+0.79
4.432	„	53.69	−0.08
4.485	„	54.36	+0.59
4.455	„	53.99	+0.22

Summary

1. In order to ascertain the conditions essential for the precipitation of phosphoric acid quantitatively as ammonium phosphomolybdate, the influence on the reaction of
   a) Temperature
   b) Concentration of nitric acid
   c) Amount of ammonium nitrate
   d) Amount of ammonium molybdate
   e) Quantity of the phosphate taken for analysis were examined.
2. The composition of ammonium phosphomolybdate after thorough washing was determined, and the behaviour of anhydrous ammonium phosphomolybdate both in the open air and in desiccators was minutely examined. As a consequence of this, all the points concerning its dehydration and its cooling after ignition were made clear.
3. The sensibility of the reaction in which phosphoric acid is precipitated as ammonium phosphomolybdate was calculated.
4. The influence of various acids and salts on the precipitation of ammonium phosphomolybdate was closely studied.
5. As the result of the investigation the method of determining phosphoric acid as ammonium phosphomolybdate was greatly improved, making it, for the first time, practically applicable.
6. The volumetric method hitherto proposed for determining phosphoric acid precipitated as ammonium phosphomolybdate was carefully traced, and an improved method giving an accurate result not inferior to the gravimetric method was also established.

The writer wishes here to express his deep gratitude toward Professor Motooki Matsui for his kind guidance and encouragement throughout this investigation.

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